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FEASIBILITY STUDY FOR ADAPTING
PRESENT COMBUSTION SOURCE
CONTINUOUS MONITORING SYSTEMS
TO HAZARDOUS WASTE INCINERATORS
Volume 1. Adaptability Study and
Guidelines Document

Prepared for

Office of Solid Waste

Prepared by

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Laboratory
Research Triangle Park NC 27711

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FEASIBILITY STUDY FOR ADAPTING PRESENT COMBUSTION SOURCE CONTINUOUS MONITORING SYSTEMS TO HAZARDOUS WASTE INCINERATORS

Volume 1. Adaptability Study and Guidelines Document

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ABSTRACT

The U.S. Environmental Protection Agency is sponsoring research programs to investigate sampling and analysis methods for hazardous waste incineration. These investigations are focused upon the adaptation of existing methods for identifying and quantifying those constituents listed in 40 CFR 261 of the regulations. As part of this program, the adaptability of existing continuous emission monitors systems (CEMS) to hazardous waste incineration sources was investigated. Measurement categories of interest include SO_2, SO_3, NO_x, CO, CO_2, O_2, HCl, and organic materials. This report focuses on commercially available sample conditioning and measurement systems, and presents the results of this adaptability study in the form of a guidelines document to be used by agency and industry personnel.

The results of this study indicate that commercially available extractive continuous monitors can be adapted to incinerators through proper sample conditioning. Conventional sample conditioning systems that dry and remove particulate matter from the sample gas should be constructed to withstand HCl gas concentrations of up to 17 percent v/v and temperatures reaching 1700°C (3000°F). Presently available continuous monitoring instrumentation provides the ranges and sensitivities needed to accurately measure concentrations of the organic and inorganic components of interest.

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SECTION 1

SUMMARY

BACKGROUND

The purpose of this document is to determine the adaptability of commercially available continuous emission monitors to hazardous waste incinerators. In addition, the intent is to provide background information and evaluation criteria for selecting and designing a monitoring system for a commerical hazardous waste incinerator.

An assessment concerning the "state-of-the-art," the deficiencies, and shortcomings of the present instrumentation and suggested development areas are presented. This work included the following tasks:

- Review of vendor product information sheets.
- Review of incineration technology and available incinerator test data.
- Evaluation of commercially available monitoring equipment.
- Identification of deficiencies.
- Preparations for an evaluation of the equipment in a field test.

RESULTS

Hazardous waste incinerators can be monitored by available ambient and stack monitoring instrumentation through proper choice of conditioning system design and instrument range. Extractive instruments are available that provide the sensitivity, stability, and specificity necessary to accurately monitor the performance of the incinerator and the control system. The following tables provide a summary of the expected flue gas parameters and conditioning requirements for three locations in the incinerator: the combustion chamber, before the air pollution control device, and after the air pollution control device. Table 1 provides a summary of the expected parameter concentration ranges and the available instrumentation ranges. Table 2 is a summary of the conditioning requirements for each general instrument type. Table 3 provides a summary of the types of instruments available for monitoring a specific pollutant with one important advantage and disadvantage listed for each type.

TABLE 1. SUMMARY OF CONCENTRATION RANGES

Parameter	Expected Concentration Range			Available range*
	Combustion zone	Before control device	After control device	
O_2	4 - 13%	4 - 13%	5 - 14%	0 - 25%
CO_2	4 - 17%	4 - 17%	2 - 12%	0 - 21%
CO	0 - 100 ppm	0 - 100 ppm	0 - 100 ppm	0 - 5000 ppm
NO_x	0 - 5000 ppm	0 - 5000 ppm	0 - 4000 ppm	0 - 10000 ppm
SO_2	0 - 5000 ppm	0 - 5000 ppm	0 - 4000 ppm	0 - 5000 ppm
SO_3	0 - 100 ppm	0 - 100 ppm	0 - 100 ppm	0 - 50 ppm
HCl	0 - 17%	0 - 17%	0 - 1000 ppm	100 - 10000 ppm
Organic Compounds	0 - 100 ppm	0 - 100 ppm	0 - 50 ppm	0 - 100 ppm

*For available instruments only, other ranges possible through dilution.

TABLE 2. SUMMARY OF SAMPLE CONDITIONING REQUIREMENTS

Measurement type	General conditioning requirements*
Chemiluminescence	Moisture
Colorimetry	Particulate
Coulometry	Particulate
Electrical Conductivity	Acid Gas
Flame Photometry	Particulate
Fluorescence/Luminescence	Moisture
Gas Chromatography	Particulate, Acid Gas
Infrared Absorption	Moisture
Mass Spectrometry	Acid Gas
Paramagnetism	None
Polarography	Particulate
Thermal Conductivity	Acid Gas
Ultraviolet Absorption	Particulate

*All extractive analyzers, except paramagnetic, require control of sample flow rate, pressure, and temperature/dew point to insure stability. Particular sensitivity to moisture, particulate, and other constituents are presented.

TABLE 3. SUMMARY OF POLLUTANT ANALYZERS

Pollutant	Monitor type	One advantage	One disadvantage
O_2	Paramagnetic	No conditioning needed	Needs cleaning often
CO_2	NDIR	Quick response	Sensitive to moisture
CO	NDIR	Quick response	Sensitive to moisture
NO_x	Chemiluminescent	Accuracy	Flow and pressure sensitive
SO_2	Flame photometry	High sensitivity	Narrow range requires dilution
	Fluorescence	Interference free	Quenching problems
	NDUV	Not sensitive to particulate	High operating temperature
SO_3	Colorimetric	Selectivity	Narrow range requires dilution
Organic Compounds	Gas chromatography (FID)	Broad linear range	Sensitive to corrosion
	Gas chromatography (ECD)	High sensitivity	Sensitive to corrosion
	Gas chromatography (PID)	Nondestructive	Low selectively
	IR Absorption	Compound specific	Low selectivity
	UV Absorption	Compound specific	Low selectivity
	GC/MS	Ultimate identification	Cost

High temperatures, particulate concentrations, and moisture contents are the important considerations when designing a conditioning system for the combustion zone monitoring locations. Acid gases (HCl) also require consideration; however, removal of moisture reduces the corrosive effects of acidic species. Acid gas, particulate, and moisture concentrations are important considerations for sampling locations before and after the pollution control device. Different parameter monitors require different conditioning measures; however, for ensured stability and reliability, the conditioning system should remove essentially all particulate matter, acid mists, condensed aerosols, and water droplets without affecting analyte integrity. Ideally, the conditioning system should only require weekly maintenance and use a minimum of expendable materials and reagents. A series of coarse and fine filters, condensation traps, and acid traps would require design details specific to each site. The effects on sample components can be defined for the range of constituents expected to be present. As more information becomes available, previously unknown effects may be discovered.

CONCLUSIONS

The sample conditioning system, if properly designed and maintained, will allow adaption of commercially available continuous gas monitors to hazardous waste incinerators. Conventional combustion and ambient monitors provide the appropriate ranges and sensitivities considering present performance requirements and anticipated concentration ranges. High concentrations of HCl gas and moisture are prime considerations in the design of a sample conditioning system. Temperatures of up to 1700°C in the combustion zone monitoring location also require consideration when selecting materials of construction. Ceramics and Hastelloy or Inconel steels are the construction materials of choice. Conditioning system designs should include an extractive probe and coarse filter followed by a moisture trap, fine filter, and a drying step prior to instrumental sample analysis. In some cases, acid gas concentrations can be reduced without affecting the sample constituents. More data is needed to establish the effects of typical acid gas removal mechanisms (by bubbler, absorber) on the integrity of SO_x, NO_x and organic species.

SECTION 2

INTRODUCTION

BACKGROUND

Proper disposal of hazardous wastes is one of the key environmental problems of this decade. To address this problem, the United States Congress in 1976 passed Federal Law 94-580, the Resource Conservation and Recovery Act (RCRA). Regulations promulgated under the authority of this legislation establishes the framework for a strong federal hazardous waste management program.[1] These regulations define those wastes that are hazardous and set standards for waste generators, transporters, and hazardous waste management facilities. In addition, the hazardous waste regulations set forth applicable physical, chemical, biological, and thermal processes that can be used to treat hazardous wastes.

Disposal of hazardous wastes is limited to essentially four options: ocean dumping, deep well injection, landfilling, and incineration. These processes were used to dispose of an estimated 57 million metric tons of hazardous wastes generated in 1980.[2] The choice of disposal method depends on several factors, including: the amount of waste to be handled, the composition and heat content of the waste, the availability of suitable local disposal sites, and the overall disposal costs.

Incineration is emerging as an especially attractive disposal technology for several reasons. These include:[2]

- Toxic components of hazardous wastes can be destroyed compounds or, at least converted to less harmful compounds.
- Incineration provides for the ultimate disposal of hazardous wastes eliminating the possibility of problems resurfacing in the future.
- The volume of hazardous waste is greatly reduced by incineration.
- Heat recovery makes it possible to recover some of the energy produced by the combustion process.

The U.S. Environmental Protection Agency (EPA) estimates that in 1979 only 5 percent of the total hazardous waste stream in the United States was disposed of by incineration, yet 60 percent of the total wastes could have been successfully destroyed using current incinerator technology.[2]

As a result of the emergence of incineration as a viable means of waste disposal, the Industrial Environmental Research Laboratory at Cincinnati (IERL-CINN) is administering an overall incineration investigation effort. This effort is focused on such areas as incineration chemistry, incinerator technology, sampling/monitoring methods, process surveillance, and quality assurance. Each of these areas are under investigation by IERL CINN with support from the Environmental Monitoring Systems Laboratory at Las Vegas (EMSL-LV) and the Industrial Environmental Research Laboratory located at Research Triangle Park, North Carolina (IERL-RTP).

In support of the IERL-CINN incineration program, IERL-RTP initiated a program to investigate sampling and analytical methods. These investigations are focused upon the adaptation of existing methods for identifying and quantifying the components listed in regulations for hazardous waste management under Subtitle C of 40 CFR 261.

OBJECTIVES AND APPROACH

This task investigates the areas of inorganic and organic continuous monitoring. The purpose of the task is to evaluate the feasability of adapting commercially available extractive continuous emissions monitoring systems (CEMS) for use on hazardous waste incinerator sources and to provide a user's guidelines manual to assist in the selection of monitoring equipment. The investigation is restricted to instrumentation for measuring the following species:

SO_2, NO_x, CO, CO_2, O_2, HCl, and hydrocarbons.

The work assignment was divided into two subtasks. An initial engineering assessment of current incinerator technology was conducted to define the environment in which a hazardous waste incinerator CSM system would operate. Ranges of expected temperatures, pressures, and flue gas constituents were developed for the three generic regions within an incinerator system; the combustion zone, before the air pollution control device, and after the air pollution control device.

The second subtask involved determining the adaptability of available measurement systems for the three sample locations. Principles of sample conditioning methods and inorganic and organic analyzer detection techniques were reviewed. A survey of available equipment was conducted by contacting instrumentation vendors and operators or owners of commercial hazardous waste incinerators.

This two-volume report is a combination equipment review and guidelines user's manual and a compilation of the incinerator design data, engineering evaluations, and data from which the expected flue gas characteristics were determined. Section 3 contains a summary of Volume II information on incineration, wastes, control devices, and expected concentration ranges of the parameters of interest. Section 4 introduces concepts important to monitoring system design and presents details of conditioning system components. Section 5 discusses operating principles for inorganic and organic species continuous monitoring. Section 6 summarizes the applicability of

conditioning methods and the various analyzers for hazardous waste incinerators.

Section 2 of Volume II presents an analysis of the characteristics of RCRA listed hazardous wastes. Section 3 introduces data on the design and performance characteristics of three types of incinerators--liquid injection, rotary kiln, and fluidized bed. Control device information is presented in Section 4 and a detailed summary of the conditions and concentrations to be expected in the three zones of interest is presented in Section 5. The pertinent conclusions are presented in the final section of Volume II.

SECTION 3

MONITORING CONDITIONS AND APPLICATIONS

The environment in which a hazardous waste CEM operates is unlike that of other combustion systems. The wide variation in composition of materials classified as hazardous, the unlimited combinations in which these materials may be mixed and burned, and the varying combustion characteristics of the individual wastes result in an environment that can change substantially from site to site and burn to burn. Volume II of this report presents an analysis of current incinerator types and emission control devices and establishes ranges of expected incinerator conditions and flue gas concentrations in the three monitoring zones of interest. This section presents a summary of the findings presented in Volume II and introduces assessment criteria for selecting a CEM system.

OPERATING CONDITIONS

The flue gas composition of a hazardous waste incinerator is largely dependent upon the composition of the waste feed material. Approximately 90 percent of the hazardous waste constituents listed in Appendix VIII of 40 CFR Part 261 are organic, and if properly combusted, will oxidize to primarily carbon dioxide and water. Sulfur oxides will be formed in proportion to the weight of sulfur in the feed material and nitrogen oxide concentrations in the flue gas are dependent upon both feed material composition (fuel NO_x) and incinerator operating temperature (thermal NO_x). Chlorinated compounds, when incinerated, form both free chlorine and hydrogen chloride. The latter predominates when excess hydrogen is provided. The same holds true for the other halogens. The incineration of certain materials including metals and some organics is avoided, when possible, due to maintenance and air pollution considerations. Certain complex hazardous wastes may form extremely toxic by-products if not completely combusted. Hazardous wastes are blended so that combustion is as self-supporting as possible and auxiliary fuel requirements are kept at a minimum. Blending of waste streams is used also to minimize the concentrations of materials which are difficult to incinerate.

Incinerator operating conditions of importance when specifying CEMs include the temperature, moisture content, concentration of carbon dioxide, oxygen, carbon monoxide, sulfur oxides (SO_x), hydrogen chloride (HCl), and nitrogen oxides (NO_x) in the gas stream. The concentrations of organic materials in a hazardous waste incinerator gas stream are largely unknown. A range of values for the known parameters is given for three incinerator types in Tables 4, 5, and 6. These ranges were based on engineering evaluations of

TABLE 4. ROTARY KILN INCINERATOR MONITORING PARAMETERS

	Temperature °F	Pressure in W.G.	O_2 %	CO_2 %	CO ppm	H_2O %	SO_2 ppm	HCl %	NO_x ppm
Combustion Zone	1300-2500	-0.5 to +2.0	8-12	4-10	0-100	3-15	0-1500	0-2	0-2000
Pre APC Device	150-600	-2 to -8	9-12	4-10	0-50	40-50	0-1500	0-2	0-2000
Post APC Device	140-535	-2 to +2	10-14	2-8	0-50	3-65	0-1200	0-0.04	0-1600

TABLE 5. LIQUID INJECTION INCINERATOR MONITORING PARAMETERS

	Temperature °F	Pressure in W.G.	O_2 %	CO_2 %	CO ppm	H_2O %	SO_2 ppm	HCl %	NO_x ppm
Combustion Zone	1200-2900	-4 to +10	4-9	8-16	0-5000	5-20	0-5000	0-7	0-5000
Pre APC Device	150-600	-4 to +10	4-9	8-16	0-100	40-60	0-5000	0-7	0-5000
Post APC Device	140-535	-2 to +2	6-10	6-11	0-100	5-60	0-4000	0-0.04	0-4000

TABLE 6. FLUIDIZED BED INCINERATOR MONITORING PARAMETERS

	Temperature °F	Pressure in W.G.	O_2 %	CO_2 %	CO ppm	H_2O %	SO_2 ppm	HCl %	NO_x ppm
Combustion Zone	800-1800	-2 to +1	2-8	10-17	0-100	5-25	0-1000	0-1	0-1500
Pre APC Device	150-600	-2 to +1	2-8	10-17	0-50	5-65	0-1000	0-1	0-1500
Post APC Device	140-535	-2 to +2	5-9	7-12	0-50	5-63	0-800	0-0.04	0-1200

the process under consideration and the types and compositions of hazardous wastes that may be burned in each incinerator. Where possible, published test data were used. In certain cases, such as the pre-air pollution control device zone, there are no published test results and only engineering estimates can be given. In other cases, such as combustion zone monitoring, the few test results that are available have been obtained during the combustion of hard-to-incinerate wastes such as PCBs and herbicide orange. The operating parameters recorded during these tests may be more severe than (and not necessarily representative of) typical hazardous waste incineration efforts. Nevertheless, where data were available, they were used to develop the presented ranges.

The reported monitoring parameter ranges are intended to provide a minimum and maximum for expected gas conditions. They should include most, but not necessarily all, conditions that may be experienced in a hazardous waste burn. More detailed breakdowns are provided in Volume II. Individual incinerator operators may decide to operate at higher temperatures or greater oxygen concentrations (excess air rates) than presented here to ensure complete destruction of the waste being incinerated. These situations were not prejudged in the establishment of a range for each parameter. In like fashion, the range of pollutant concentrations may be exceeded if a relatively pure stream of a single pollutant compound; i.e., hydrogen sulfide, is incinerated. Again it was judged that such an event is unlikely, and therefore should not be used to define an unreasonably high maximum concentration.

MONITORING APPLICATIONS

The choice of a conditioning system and continuous gas analyzers is influenced by the concentration ranges of the species of interest in the incinerator system. The conditioning system must be designed and constructed to withstand the high temperature corrosive environment of the combustion zone as well as the wet, cool environment after a scrubber. At present, federal regulations specify temperature, pressure, CO, and O_2 ranges as indicators of destruction efficiency. The performance specifications for these continuous analyzers are defined and should be used as a guide in selecting instruments for the other parameters of interest.

Three monitoring zones are considered throughout this report to address four basic goals of hazardous waste incinerator emission monitoring. The most important goal is the documentation of pollutant destruction efficiency. With monitored waste feed rates and compositions, continuous monitors in the combustion zone would enable destruction efficiencies to be determined. A second goal is the continuous documentation of control device removal efficiency. Comparing pollutant concentrations measured before and after the pollution control device would allow real time monitoring of efficiency. The third goal is the continuous documentation of the emissions to the environment. The compliance status of the source, with respect to applicable air pollution control regulations, would be more fully documented through continuous monitoring in addition to source performance testing conducted periodically. The fourth goal is to provide the source operator with process information to aid in determinations of maintenance needs of the incinerator and pollution control equipment.

SECTION 4

CONCEPTS OF SAMPLE CONDITIONING

Systems used to measure the performance of a hazardous waste incinerator must be equipped to measure criteria pollutants (NO_x, SO_2, CO, etc.) and selected organic species under a wide range of sampling conditions. Depending on the incineration system and the sampling point location, temperature extremes of up to 1700°C (3000°F), moisture levels approaching 65 percent, and acid gas levels that simultaneously reach 17 percent by volume per acid component could be encountered. The CEM conditioning system must be sufficiently versatile to accommodate the hot, corrosive atmosphere of the combustion zone as well as the cooler, wet sampling conditions in the exhaust stack.

The objective of sample conditioning is to provide an unadulterated sample that is compatible with the analyzers in use. Maintaining the integrity of the inorganic and organic analytes while removing compounds that are interferences or are harmful to the instrument (i.e., HCl gas) is difficult when large changes in the physical state of the sample are required. The three sample zones represent a wide cross section of temperatures, pressures, moisture contents, acid gas contents, and particulate loadings. Ideally, one inorganic and one organic sample conditioning system could be used for all three locations through proper system design and choice of analyzers. Even more desirable is the ability of this same conditioning system to be used for both inorganic and organic species of interest to minimize the capital investment required by the incinerator owner.

Sample conditioning equipment is defined as all flow related equipment preceeding the continuous gas analyzers. The following subsystems are integral parts of the sample conditioning equipment:

- Probe/preconditioning module/heat traced transport lines
- Flow control/pumping system
- Distribution control system

Flue gas is typically passed through a heated probe and into a conditioning module where large particulate, acid mist, high boiling compounds, and moisture removal is accomplished. From this point the sample gas is transported to the continuous gas analyzers through transport tubing, flow control systems, and various valving systems. Both calibration gases and sample gases are passed through a distribution control panel. It is desirable

to route calibration gases through the probe inlet for complete system calibration. The operating requirements of a particular analyzer play an important part in the design of the sample interface system. Requirements that must be considered are as follows:

- Sample temperature, pressure, and flow rate
- Sample particulate and moisture levels
- Interfering species in the gas stream
- Chemical corrosion of interface surfaces.

Besides maintaining sample integrity, other important considerations are maintainability and effects on response time. For effective long term operation, the conditioning systems should only require minimal routine weekly maintenance. The conditioning should be relatively quick, ideally less than 1 minute, in order to provide a sample as close to "real-time" as possible. Conditioning systems have been designed and manufactured on a case-by-case basis where the range of wastes to be incinerated was well defined. Some degree of adaptation of any system must be done by a user. Specific conditioning requirements of each continuous monitor, if known, will be referenced in the appropriate instrument sections. Conditioning methods and the advantages and limitations of each method as applied to measurement of inorganic and organic species will be discussed in the following sections.

PARTICULATE REMOVAL

Most extractive gas analyzers and organic species analyzers require the removal of particulate matter prior to sample analysis. In addition, particulate matter can clog sample lines and shorten the life of the sample pump. Particles can be removed by coarse and fine filters or inertial separators. There are numerous types of filter bodies and filter elements constructed of both organic and inorganic materials. Selection is based on particle size and stream loading factors, as well as the nature of the analyte gases. Particles are usually removed in two stages: an initial stage (coarse filtration) and a final stage (fine filtration).

Coarse Filtration

Larger particles can be removed by passive filtration, inertial separation, or inertial filtration. Passive filtration is accomplished by placing a sintered metal filter of large surface area, typically constructed of sintered 316 stainless steel, at or near the sample stream extraction point. Sintered filters normally remove all particles that are larger than 10 to 50 micrometers. Glass, ceramic, quartz, and other metals (Carpenter 20, Hastelloy C) may also be used in sintered filters. The porous medium should be protected by a baffle to prevent excessive particulate buildup on the leading surfaces when mounted in the flue. These filters should be maintained at or above the flue gas temperature to minimize the incidence of plugging and corrosion.

Larger particles can also be removed by inertial separation. This type of coarse particulate removal can be accomplished by using a flow-through cyclone. In the cyclone, the sample gas is introduced tangentially and exhausted through the bottom. The cyclonic flow causes the particles to be accelerated toward the inner walls of the device. The sample stream is extracted from the vortex present inside the cyclone. Cyclones have a distinct particle size upper cut point dependent upon geometry, flow rate, and gas viscosity. Gases containing water droplets and/or high concentrations of large particles, would be more effectively "coarse" cleaned with a cyclone than a filter. Cyclones do not plug easily and can be cleaned using automatic blow-out systems. A disadvantage is higher cost; however, the failure rate is low. The cyclone should be maintained at or above the flue gas temperature. Many materials of construction are available.

The flow-through tube filter utilized in inertial filtration combines the techniques of passive filtration and inertial separation. The large ratio of axial to radial sample gas velocity in the tube filter prevents larger particles from impinging on the filter pore structure. Smaller particles establish a dynamic membrane on or within the porous wall, and in equilibrium with very low drag forces, effectively prevent transmission of particulate contaminants much smaller than the filter pore size. The turbulent nature of particulate laden gas flowing through the filter tends to keep the filter clean by abrasion. The flow-through tube filter can be mounted either internal or external to the stack or duct. This element would require the same high temperature materials as passive filtration and cyclone inertial separation devices.

Fine Filtration

The majority of extractive gas analyzers and organic species analyzers require almost complete removal of all particles larger than 1 micron from the sample gas stream. In order to reduce particles to this level, a low resistance, high efficiency filter is needed. Fine filtration is usually accomplished by adding a second fine filter near the analyzer inlet. Fine filters are divided into two categories: surface filters and depth filters. Surface filters remove particles from the gas stream using a porous matrix. These filters can remove particulates smaller than the actual filter pore size as a result of particulate cake buildup and electrostatic forces acting to trap smaller particles without excessive resistance. Depth filters collect particulate matter within the bulk of the material. A depth filter may consist of loosely packed fibers or relatively large diameter granules. The spun glass filter is a depth filter which when maintained at elevated temperatures (e.g., 220°F (104°C)), reliably and efficiently removes particulates as small as 0.5 micron. Spun glass, when packed to a density of 0.1 gm/cm^3 and a bed depth of at least 2 inches, can act as an inexpensive depth filter for normal gas flow rates.

Application Requirements

The corrosive constituents encountered in monitoring hazardous waste incinerators are: nitrogen oxides, sulfur dioxide, dilute to concentrated sulfuric acid (wet SO_3 or acid mist), and halogen acids (HCl, HBR, HF). An

instack filter should be fabricated of sintered metal, refractory, metallic screen, or high temperature fabrics. Ordinary steel is limited to stack temperatures below 1400°F (760°C) while 316SS is usable to 1600°F (870°C). At higher temperatures, a water-cooled probe/filter may be used or stainless steels with higher nickel compositions such as Hastelloy or Inconel.

The chemical resistance of various materials to some expected gas constituents has been collected from various sources and summarized in Table 7. Of the metals, titanium is the most resistant (and also the most expensive) followed by the nickel alloys and stainless steel alloys. Finally, the inert materials such as quartz and glass are quite resistant but the most fragile.

Studies have shown that some organic compounds adsorb onto the filtered particulate matter which result in a low bias at the instrument. The relative amounts of adsorbed material is a function of filtration temperature among other factors. Stack tests at the Marquardt liquid injection incinerator[3] were performed where combustion zone gases were cooled from 1000°C to 100°C prior to particulate filtration. Analysis of the filtered particulate was performed by extracting with methylene chloride and using instrumental IR and low resolution mass specrometry (LRMS) whereby alkyl hydrocarbons and alkyl esters of phthalic acid were found. Higher boiling point compounds not extracted by methylene chloride may also have been present. Particulate removal by filtration at elevated temperatures may prevent condensation of organic compounds, however, this poses a problem in that only coarse filters are routinely used at high temperature combustion zone sampling locations. Fine filters that remove particles smaller than one micron need to be found that will withstand 1000 to 1500°C temperatures. Filter materials must be chosen that will not catalyze additional chemical reactions. The fine filters should also be self-cleaning and only require weekly maintenance or changing since maintenance performed near the hot zones of an incinerator are dangerous procedures.

For the zones before and after the control device, distinguishing between particulate matter and condensed organic material is the major problem. As the effluent gas cools, higher boiling point compounds may condense and form aerosols. Filtering and removing these organic aerosols could only be prevented through revaporization of the sample. Analysis of these higher boiling compounds is of prime importance when determining the overall destruction efficiency. In all three zones, the affect of the filter material, binders and filtered particulate matter on passing organic compounds needs to be determined. Acid catalyzed reactions, fine particles acting as reaction sites, and numerous other possibilities exist for altering or trapping the organic compounds of interest.

The compatability of filter materials to the waste gas stream is also important. High concentrations of various organic compounds have been tested for compatability with many types of filters. Table 8 provides an indication of the chemical resistance of three general types of filters to some common organic compounds. Obviously teflon is the most inert, however, other considerations such as pressure drop, pore sizes, costs, temperature limitations and replacement frequency need to be considered when designing a

TABLE 7. CHEMICAL RESISTANCE OF MATERIALS TO EXPECTED GAS CONSTITUENTS IN HAZARDOUS WASTE INCINERATORS

	Nominal chemical composition (%)									Corrosion resistance and some physical properties																
Material	Ni	Cr	Mo	Fe	Si	C	Mn	P	S	Fl	Dry CO_2	Wet CO_2	Wet Cl_2	DIL HCl	Dry HCl	HF	DIL H_2SO_4	DIL H_2SO_3	DIL HNO_3	Dry H_2S	DIL NaOH	Dry SO_2	Wet SO_2	SO_3	Temp. above 1000°F	Description
Glass					100						2	2	2	2	2	3	2	2	2	2	1	2	2	2	2	
Titanium											1	1	2	2	2	2	1	1	1	1	2	1	1	1	1	MP[a] 1300°F
Hastelloy C-276	54	15	16	5			1				1	1	1	2	1	2	1	2	1	1	2	1	1		1	MP[a] 2380°F
Inconel 625	60	21	9	5	1[b]		1[b]				1	1	3	2	2	2	2	3	3	2	2	2	3	3	1	High strength, good to 1800°F Good oxidation Resistance, good corrosion resistance
Incoloy 800	32	20		46	1[b]		1[b]						1	1	1		2	2	1						1	Good oxidation resistance resists sulfur attack, internal oxidation, scaling and corrosion, good to 1600°F
316SS	14	18	2		1	1[b]	2	1[b]			2	2	3	3	2	3	2	1	1	2	2	2	2	2	1	
Carpenter 20SS	29	20	2	43	1	1[b]	1[b]				1	1	3	3	3	2	2	1	1		2	2	2	2		
304SS	10	19			1	1[b]	2	1[b]			1	1	3	3	2	3	3	1	2	1	2	2	1	2	1	Resistant to corrosives, reducing acids, oxidizing chemicals
Incoloy 825	42	21	3	30	1[b]	1[b]	1[b]						1	1	1		1	1			2				2	MP 2500°F
Quartz					100						2	2	2	2	2	3	2	2	2	2	1	2	2	2	2	

(continued)

TABLE 7 (continued)

Material	Nominal chemical composition (%)									Corrosion resistance and some physical properties																Description
	Ni	Cr	Mo	Fe	Si	C	Mn	P	S	Fl	Dry CO_2	Wet CO_2	Wet Cl_2	DIL HCl	Dry HCl	HF	DIL H_2SO_4	DIL H_2SO_3	DIL HNO_3	Dry H_2S	DIL NaOH	Dry SO_2	Wet SO_2	SO_3	Temp. above 1000°F	
Teflon						24				76	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3	500°F
PVC											2	2					3	2	2			2			3	
Tygon											2	2					2	2	3			2			3	
Poly-ethylene											2	2					2	2	3			2			3	
Poly-propylene											2	2					2	2	2			2			3	

Source: References 4, 5, 6, 7, and 8.

Key: Excellent - 1 Acceptable - 2 Not Recommended - 3

[a]MP = melting point

[b]Values less than 1 but greter than 0.5

TABLE 8. ORGANIC SPECIES/FILTER MATERIAL COMPATABILITY

	Depth nitrocellulose	Screen polycarbonate	Porous teflon
ACIDS			
Concentrated	D	G	G
6 Normal and weaker	G	G	G
ALCOHOLS			
n-Amyl, butyl, glycerol	G	G	G
ethyl, methyl, isopropyl	D	G	G
BASES	D	D	G
CRYOGENIC GASES	G	G	G
ESTERS	D	G	G
ETHER ALCOHOLS	D	F	G
FUELS	G	G	G
HALOGENATED HYDROCARBONS			
CCl_4	G	G	G
Chloroform	G	D	G
Methylene Chloride	F	D	G
Perchloroethylene, trichloroethylene	G	F to G	G
HYDROCARBONS	G	G	G
KETONES	D	G	G
OILS	G	G	G
PHOTO RESISTS	D	G	G
SOLVENTS	G	G	G
WATER	G	G	G

G - Good
F - Fair
D - Dissolves

specific filtration system. Very low concentrations of the organic species are expected to be present, therefore, minimizing gross compatability problems; however, substantial acid gas concentrations are expected to greatly influence the choice of filter material.

ACID MIST AND HIGH BOILING COMPOUND REMOVAL

Incinerator effluent gases can contain significant quantities of acid mists and vapors. Analyzer temperatures must be kept above the acid dewpoint to prevent condensation within the analyzer. An acid mist coalescer, which is a knockout bowl of nonreactive glass or plexiglass, can be used to remove acid mist. The trap should have a drain line made of nonreactive material such as teflon, which leads to a collection bottle, treatment system, or drain. The line can have an automatic or manual drain valve. The automatic valve should dump the filter bowl when a back purge is activated. Analysis of the water or condensed sample could be performed to verify no loss of sample. The knockout bowl is maintained at a lower temperature than the gas stream. This drop in temperature through the bowl may effectively remove most of the acid mist. If cyclones or tube filters are used for the initial particulate removal, these will also remove acid mist droplets. The filter elements must be inert and should not include any binders that undergo chemical changes. One of the better materials for this purpose is polypropylene. Polypropylene is hydrophobic (repels liquid water) and is available as a yarn, fabric or a fused, porous tube. As a yarn it can be wound on a core to provide a larger surface area for coalescing acid vapors. As a fabric it should be pleated to give a larger surface area. Fiberglass yarn can be wound on a stainless steel core and, if the winding lubricant is extracted, a pure glass element can be produced. The glass element can be used at high temperature and is chemically inert. Many filter housings designed to be chemically inert, withstand high pressures, and provide visibility of the filter element can be assembled and disassembled without tools. Filter housings are designed to maintain good heat transfer. The chemical resistance of the filters and materials of construction are presented in Table 9.

Sulfuric acid mist can be removed by controlling the filter temperature. The acid dewpoint temperature, shown in Figure 1, is a function of H_2SO_4 concentration and temperature. At temperatures below 212°F (100°C), the concentration of acid as a vapor is below 0.1 ppm. Oxides of sulfur (SO_2 and SO_3) and water vapor will pass through a filter element; however sulfuric acid will condense at the dewpoint temperature.

When high boiling organic compounds exist in the gas stream, it is important that removal is accomplished to prevent condensed tar-like materials from plugging the instrument. Removal can be accomplished by condensing the compounds on either an inert substance, such as glass beads, or a disposable substance such as fiberglass. The adsorbing medium should be in an inert container. To ensure that the water in the sample is maintained in the vapor state while the high boiling compounds are removed, condensor temperatures greater than 212°F (100°C) should be used. The inert condensing surface is then cleaned or discarded periodically, which requires a bypass to an unused system. High boiling compound removal can be affected between the initial and final particulate removers.

TABLE 9. CHEMICAL RESISTANCE OF FILTERS TO EXPECTED GAS CONSTITUENTS IN HAZARDOUS WASTE INCINERATORS

Chemical	Conc. (%)	Max temp. °C.	Filter housing				Filter elements			Seals		
			SS	AN	AF	PP	SS	PP	SG	EP	VV	TFE
Acid												
HCl	1	50	NR	NR	R	R	NR	R	NR	E	R	E
HCl	10	50	NR	NR	R	R	NR	R	NR	E	R	E
HNO_2	5	80	R	R	R	R	R	R	R	R	R	E
H_2SO_4	1	80	NR	F	R	R	NR	R	NR	R	R	E
H_2SO_4	5	80	NR	F	R	R	NR	R	NR	R	R	E
Gases												
NH_3	10	80	R	R	R	R	R	R	R	R	R	E
NO_2	1	80	R	R	R	R	R	R	R	R	R	E
SO_2	5	80	F	R	R	R	F	R	R	R	R	E
H_2S	10	80	R	R	R	R	R	R	R	R	R	E
Cl_2	1	80	NR	NR	R	R	NR	R	NR	R	R	E
Cl_2	100	80	NR	NR	F	R	NR	R	NR	F	R	E
O_3	1	80	R	R	F	R	R	R	R	F	R	E

SS - Stainless Steel
AN - Aluminum - Nickel
AF - Aluminum - Teflon
PP - Polypropylene
SG - Stainless Steel and Fiberglass
EP - Ethylene - Propylene Rubber
VV - Viton - Rubber
TFE - Teflon

NR - Not Recommended
P - Poor
F - Fair
R - Recommended
E - Excellent

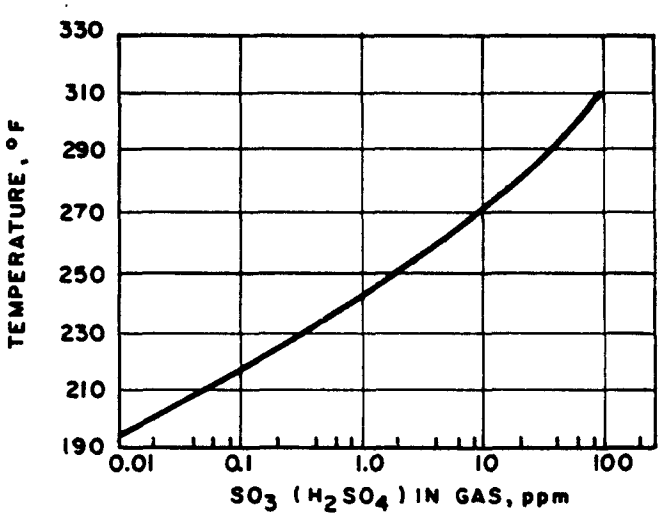

Figure 1. Plot of H_2SO_4 vapor versus temperature.

Acid vapors and mists adversely affect the lifetime of the majority presently available organic species instrumentation. Corrosion, cracking, etching, salt formation and deposition can all lead to premature instrument failure. The anticipated high levels of inorganic acid gases should be reduced in the conditioning system without removal of organic acids and other organic compounds of interest. Removing acid gases is possible by bubbling the gas through a caustic solution, by lowering the temperature to well below the acid gas dew point or by using a selective membrane or a dry alkaline absorbent. The effects of these treatments on the integrity of the organic species of interest will need to be fully documented. Determining which of the available methods is suitable for organic species monitoring is dependent in part on the organic species of interest. C_1-C_4 hydrocarbons are not appreciably soluble in water or basic solutions and do not condense at ambient temperatures. A simple water bubbler containing sodium hydroxide could be used to neutralize acid gases when analyzing for these hydrocarbons. Organic acids, aromatics and other soluble or acidic organic species would be trapped in the caustic solution, therefore, this method would not be applicable if these compounds were to be analyzed.

Ion exchange resins which are specific for inorganic acids have been developed. The use of these resins for continuous monitoring applications has not been well documented and the quantitative recovery of organic species should be determined prior to use. No commercially available conditioning systems for organic instrumentation using ion exchange columns were found. A variation of this, the use of precolumns in a chromatograph, has been in wide usage in hydrocarbon continuous analyzers where a timed backflush valve is used. After a sample is injected into the GC, a timer is used to activate a backflush of the precolumn after elution of the species of interest. This conditioning method of sorts prevents other species from entering the detector and unnecessarily lengthening the analysis time. This same theory may be used to remove unwanted inorganic gases and acids if the appropriate materials are selected.

A semi-continuous conditioning method for organics using Tenax, XAD or similar adsorbant resins has been developed primarily to concentrate a sample for GC/MS analysis. By automating a typical manual sampling method, a conditioning method has been developed wherein the sample is passed through one to two or more adsorbant tubes for a preset length of time; a fresh trap is then cycled into place while desorbing the first trap of organic material. The resin trap organic materials while allowing inorganic gases (acids) to pass through. This conditioning method mimics several EPA methods involving condensation traps with adsorbants, most notably Level 1 SASS measurements. This method has not been used in continuous monitoring applications, but is a promising area for future research. The effect of HCl concentration on the adsorption efficiency of the resin should be investigated since the acidification of the resin may prevent collection of neutral or alkaline organic species. Cycle times are available that allow 2 minute to 2 hour adsorption times with thermal desorption times on the order of 1 minute. Solvent desorption systems are available. This purge and trap procedure would be applicable for parts per trillion sensitivity since no continuous monitoring instrumentation is presently available for use in this concentration range. Analysis of the concentrated sample requires a trade-off

with time, the greater adsorption times providing a higher concentration sample with decreasing levels of "real time."

MOISTURE REMOVAL

Incinerator stack gases can contain significant quantities of water vapor. For some analyzers which are insensitive to water vapor and can operate at higher temperatures (e.g. the UV instruments) the problems of moisture removal can be avoided by keeping the temperature of the sample above the dewpoint. This requires heated sample lines, heated filters, and possibly a heated sample pump. Use of a totally heated system appears to be inconsistent with the criteria for a minimum design.

For analyzers which cannot operate at very high temperatures, moisture removal is a necessity. There are a variety of methods for moisture handling and removal. The methods are condensation, permeation distillation, membrane separation, and air dilution.

Condensation

Moisture removal is most readily accomplished by allowing the sample to cool. Refrigerated condensers are available for cooling sample gas streams. A typical condensation system design is shown in Figure 2. This design requires a primary and secondary condenser to decrease the moisture level to less than 1 percent (v/v). In the primary condenser, the moisture level is reduced to approximately 2 to 3 percent. Because this condenser is at an absolute pressure that is less than the ambient pressure, the condensation process is not as efficient as it would if the condenser pressure were greater than ambient pressure. Final moisture removal is accomplished by passing the pump effluent under pressure through the secondary condenser. The increased pressure enhances the condensation process by raising the vapor pressure of moisture and increasing the residence time in the coil. Sample gas existing the secondary condenser typically contains moisture levels approaching 0 percent.

Permeation Distillation

Permeation dryers have been used with success in drying combustion stack gases.[4] The dryer uses a semipermeable membrane as a water removal system, and a dry gas for continuous regeneration. Specifically, the dryer is a bundle of membrane tubes with a common header in a shell and tube configuration. Openings adjacent to the sample inlet and product outlet (Figure 3) are provided for the dry gas. The wet gas sample flows through the tubes, and the dry gas flows countercurrent to the shell which permits water vapor to be purged and transported through the tubing. Water diffuses to the dry side of the bundle by a simple diffusion mechanism where the natural tendency is to equalize concentrations on both sides of the membrane. The efficiency of the dryer at constant temperature and humidity is based on the amount of tubing in the shell and the sample and purge flow pressures.

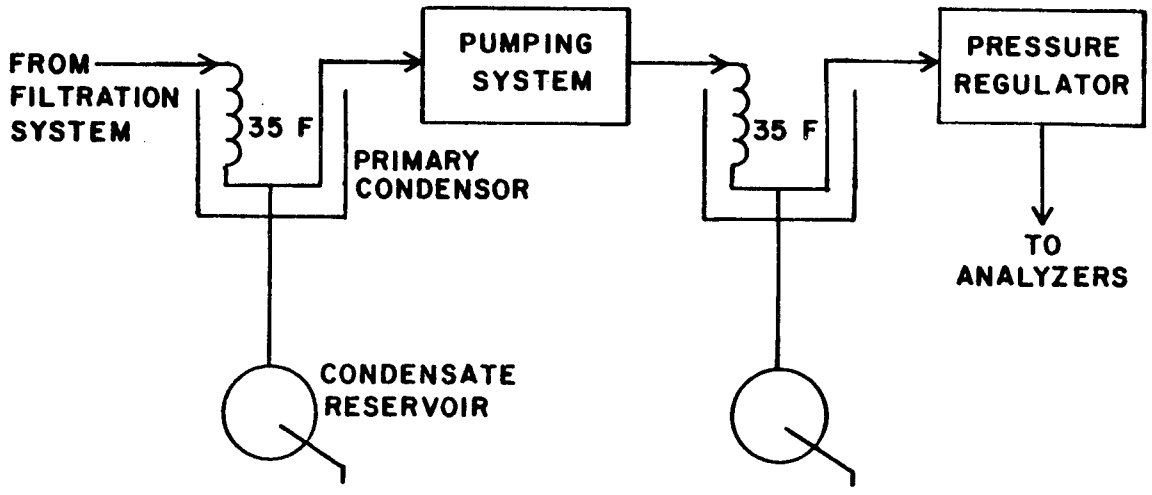

Figure 2. Moisture removal using condensation.

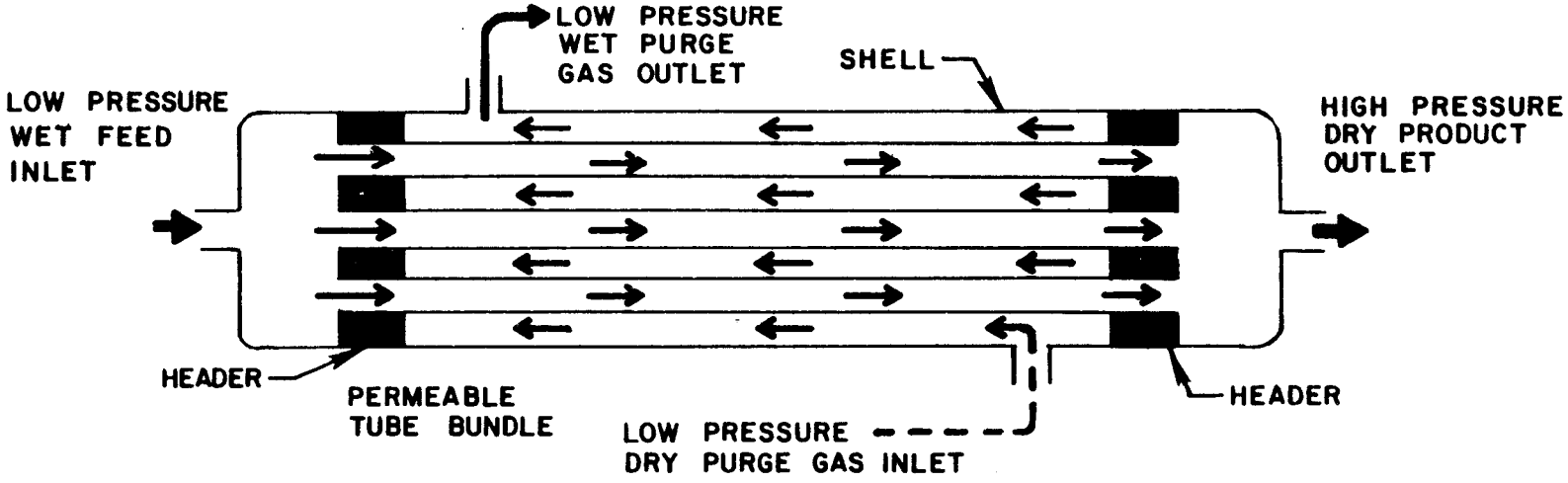

Figure 3. Typical permeable distillation membrane dryer.[9]

Membrane Separation

Membrane separation by reverse osmosis is a newly applied gas/liquid separation technology. A membrane that is selective to certain components of a gas or liquid stream will allow passage through while one or more other components cannot do so. The semipermeable membrane is sometimes used with pressure to reverse the natural tendency of osmosis to equalize concentrations. The flow of material from the least concentrated to the more concentrated phase or the tendency to dilute concentration is reverse osmosis. Research is underway to separate CO_2 from methane by this method.[5] Other gases could be selectively permeated.

Air Dilution

The sample can be diluted in the probe with a clean dry non-reactive gas in order to overcome instrument range problems or to minimize corrosion. This will generally be dry instrument air which contains virtually none of the contaminants to be measured. The dilution ratio selected at the probe is generally greater than 70:1 to reduce the dewpoint of the sample for transport in unheated tubing to the ambient air analyzers. With ambient air as the diluent, SO_2, CO, NO, NO_2, Hydrocarbons, and CO_2 can be measured. Calibrations are generally made using dilution air as zero air.

Dilution ratios must be selected by calculation using the dilution range desired and the measurement range of the analyzer. Typically, a dilution system has dilution ratios ranging from 12:1 to 22,500:1 or larger with a double dilution technique. The analyzers, however, should have at least 20:1 rangeability or larger. A vacuum is drawn on a stack gas sample continuously by an ejector pump, sometimes mounted inside the stack probe. The instrument air stream (pressurized air) with an adjustable flow creates a vacuum in the space between the primary and secondary nozzle of the ejector pump. The vacuum is used to transport the stack gas through a critical orifice also sometimes mounted inside the stack probe. The critical orifice defines the sample flow at all pressures below the critical pressure. Control flow will be reached when the vacuum in the ejector pump ranges from 0 to 0.34 bar (0 to 35 cm Hg). Within certain limits the flow through the critical orifice depends on the pressure in the stack. Flow also depends on the viscosity of gas which will vary with process conditions and moisture content. A sample pressure variation of 10 mbar typically changes the flow of diluted sample by 1 percent. As the flow of dilution air must be adjusted by the operator, the dilution ratio can be varied between certain limits. The diluted sample stream is directed to an emission monitor through a tube in the umbilical cable.

Wet Measurements

Not removing the water contained in the gas is desirable when analyzing for easily condensed or water soluble components. There are two methods for keeping water in the vapor phase in a gas stream: heating and pressure reduction. Heating a stream above 212° (100°C) will keep water in the vapor phases if the total pressure is near atmospheric. By dropping the pressure of the gas stream, a lower condensation temperature can be realized. Figure 4

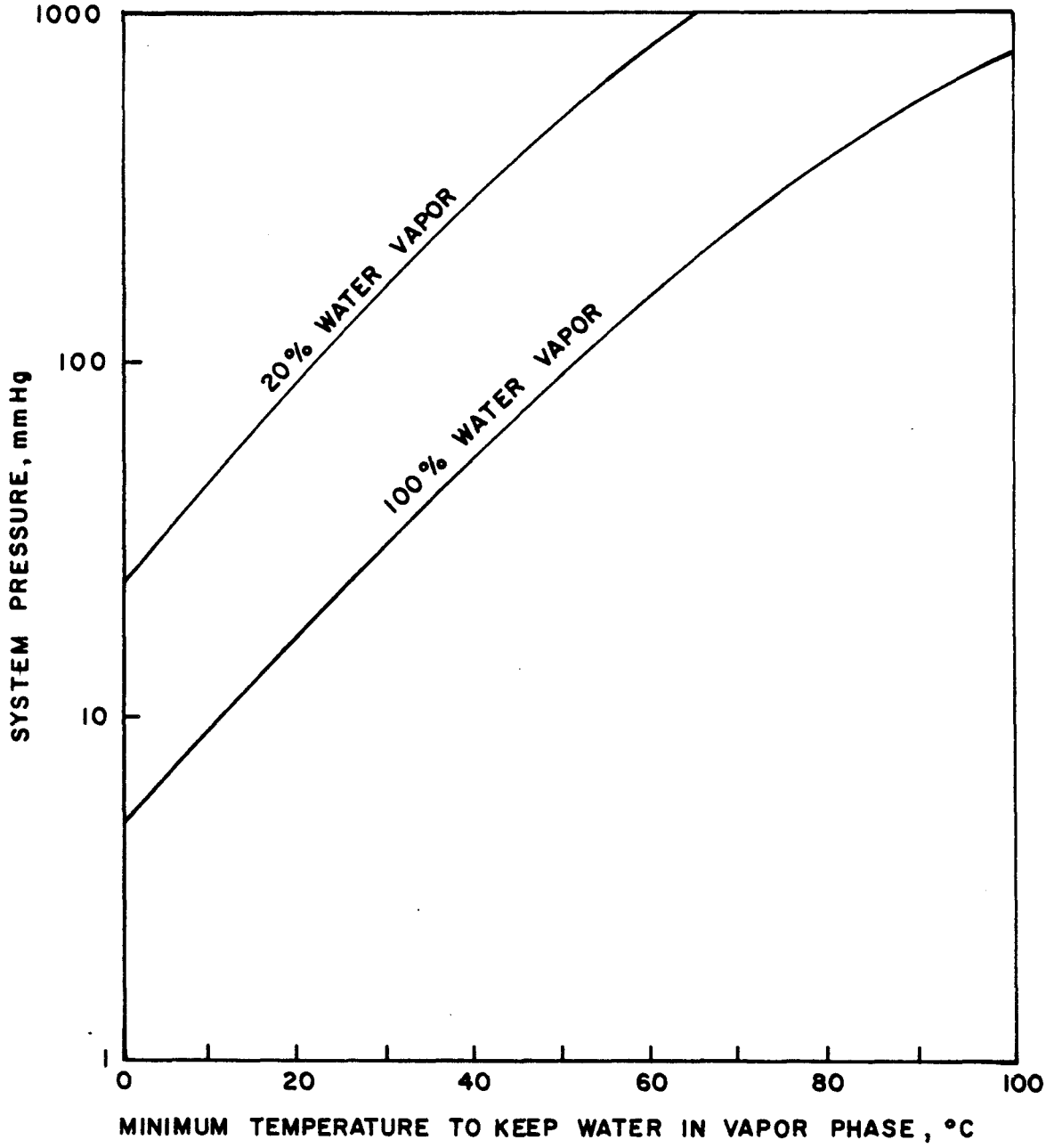

Figure 4. Condensation pressure.

shows the relationship for temperature required to keep water in the vapor phase as a function of pressure. The application of this method is to heat the gaseous sample above the dewpoint until the pressure can be reduced to a level where condensation will not occur at room temperature. Once the appropriate pressure is achieved, no further heating would be required.

Applications and Problems

Some commercially available systems maintain the sample above the dewpoint. This is done primarily to avoid solubility losses of the species being measured. Some instruments in particular are analytically sensitive to water vapor. This sensitivity can be circumvented by the use of optical filters within the analyzer, by removal of water vapor, or by the use of constant water concentration in both the sample and calibration gases. It is important to determine the amount of water vapor that must be removed in order to operate within the accuracy limits of the analyzers. The effect of water vapor will increase as lower concentrations of SO_2 or NO_x are measured by an NDIR instrument. A typical water sensitivity for an NDIR instrument is on the order of 20,000 to 1. That is, 20,000 ppm water registers as 1 ppm pollutant on the analyzer. The use of a constant moisture level in both the sample and calibration gases is a method of minimizing the effects of water vapor. This is done as simply by condensation or the use of desiccants. There is a possibility of interactions with constituents of the sample stream other than water. Some loss of SO_2 on dessicant materials has been observed.[6] Dessicants are not considered as a viable water removal mechanism for most analyzers.

Permeation distillation has been used with some success as mentioned previously. Some advantages for permeation dryers are listed:

- materials of construction do not come into contact with liquid condensate and therefore are less prone to corrosion;
- a condensate trap is not required for removal of liquid;
- there is little possibility of sample loss by solution in liquid condensate.

Some disadvantages are:

- particulate plugging;
- a vacuum pump and controls must be maintained on the shell side of the dryer or
- a regulated supply of dry purge air must be used.

If the dryer is located in the instrument house, the entire sample line must be kept above the sample dewpoint and if it is located in the vicinity of the stack, the heat tracing problem is reduced but the accessories and controls (vacuum pump, pressure gauge, flow meter and valve) would be in a less accessible location. Long sample lines could be run to and from the dryer but these are inconvenient.

Overriding advantages for condensation systems include the simplicity of operation and minimal need for heat traced sample lines. The disadvantages of the condensation method include:

- corrosion on condenser parts;
- solubility losses of constituents from gas stream; and
- response time lags due to the large volume of the condensate trap;
- refrigeration compressors are expensive to purchase, operate and maintain.

The air dilution sampling system is a particularly effective method of sampling hot, dusty, and corrosive stack gases. This systems advantages include:

- condensation in the sample line is avoided;
- quick cooling and dilution of the sample avoids reactions of sample components;
- no moisture is removed by refrigeration or semipermeable membranes;
- the system has no moving parts,
- no additional heating is required;
- if required, a second diluter unit can be incorporated in the sample stream for greater dilution flexibility.

Disadvantages of air dilution include capillary plugging problems, even after fine filtration.

Several methods of removing excess moisture have been discussed. A wide range of boiling points of organic species could be present in the sample gas stream, therefore, moisture removal mechanisms that lower the gas stream temperature may also remove organic species. If only lower boiling, relatively insoluble organic compounds (C_1-C_4) are to be monitored, moisture removal by any of the methods presented earlier would not seriously affect the integrity of the sample. If easily condensed organic compounds are to be analyzed, dilution methods and heating the gas sample above the dew point are methods of choice. The sample temperature must always be above the boiling point of the compound of interest. Table 10 provides example hazardous compounds classified by boiling point and Table 11 provides a listing of compound classified by solubility in water. From these two tables, one can predict some of the compounds that may be prematurely removed through condensation of moisture or temperature changes. Methods that involve no removal of water hence no inadvertent loss of condensed organic material would be preferred. No organic species analyzers are sensitive enough to allow for substantial dilution of the sample, however, several are insensitive or can be desensitized to substantial quantities of water vapor. Conditioning systems

TABLE 10. BOILING POINT RANGES OF SELECTED HAZARDOUS ORGANIC COMPOUNDS

Boiling point range		
Low boilers (60-212°F)	Medium boilers (212-400°F)	High boilers (400-600°F)
Acetone	Octane	Dodecane
Acetyl chloride	Ethyl benzene	Napthalene
Chloroform	Toluene	Fluorene
C_1-C_4 alkanes	1,1,2-trichloroethane	Trichlorobenzene
1,2-dimetyhlhydrazine	Chlorobenzene	Benzothiophene
2-nitropropane	Trichlorohydrin	Biphenyl
Tetrachloromethane	Phenol	Diphenyl sulfide

TABLE 11. WATER SOLUBILITIES OF SELECTED HAZARDOUS ORGANIC COMPOUNDS

Insoluble	Soluble	Highly soluble	Miscible
Acetophenone	Acetaldehyde	Acrylamide	Acetone
Benzyl chloride	Analine	n-butyl alcohol	Dimethylamine
Dieldrin	Chlorobenzene	Chloroform	1,2 dimethyl hydrazine
Ethylmethacrylate	Cyclohexanone	Chresylic acid	Malononitrile
2-chloronaphthalene	Lead acetate	1,2 dichloropropane	Pyridine
di-n-butyl pthalate	Paraldehyde	Ethylenediamine	Acrilic acid

consisting of no moisture removal mechanisms and only heat traced lines (to 400°F) have been used routinely with flame ionization detectors. Conditioners using a membrane drying system have also been successfully used since once an equilibrium level has been reached, normal alkanes are not removed by the membrane dryer either through filtration or surface attractions. Moisture condensation, which activates the corrosiveness of HCl gases, must be prevented in order to maintain the analyzer in good order and to prevent loss of soluble compounds.

Connective Line

Gas transport or connective tubing requires certain considerations. These are as follows:

1. Tube interior-exterior diameter

2. Heat resistance

3. Chemical resistance to gases being sampled

4. Cost

Connective tubing must be sized to ensure an adequate gas flow rate and linear velocity with a reasonable pressure drop to provide good system response times. A flow rate of 2 slpm (enough to supply two gas analyzers) through 1/4 inch tubing exhibits a pressure drop between 1 and 3 mmHg per 30 meter length (depending on wall thickness). This pressure drop is quite acceptable for most sampling pumps.

Teflon and stainless steel tubing exhibit corrosion and heat resistance in addition to being chemically resistant to stack gases and acid mist. The corrosion resistance of stainless steel is enhanced by keeping gases above the dewpoint.[7] Heat traced stainless steel and teflon tubing is commercially available from several suppliers. Copper or brass could be specified for temperatures up to slightly over 400°F, providing the gas is not highly corrosive and will not be significantly affected by potential corrosion products. Aluminum has a temperature limit of about 500°F. Carbon steel tubing, generally annealed for ready bending, can go to 700°F or even 800°F when corrosion is not a problem. For higher temperatures, either type 304SS or 316SS is suitable. With carbon steel, for temperatures above 800°F, carburization can occur. At temperatures above 900°F carburization can occur in stainless steels. For highly corrosive, but moderate temperature conditions, plastic tubings and fittings are effective. Teflon, polyethylene, plasticized PVC, and nylon are available with either corrosion-resistant-metal or plastic fittings and are useful up to about 350°F. Connections for pipe may be threaded with either ordinary or modified threads to resolve leakage. Brazing and welding can be used, but crevices can form causing flow difficulties and erosion from abrasive particulate laden gases. Several designs of all-metal tubing connectors are available and in common use. These fittings utilize ferrules which are driven tightly against the tube wall to seal the connection. Fittings are available in 316 ss and brass.

As summarized in Tables 7 and 9, stainless steel is a good material for in-stack tubing. The middle grade, type 304, is used for a wide range of slightly corrosive materials. Type 316, molybdenum containing steel, is used for process chemicals, acids, bleaches and more corrosive materials. Carpenter 20 is the better of the stainless steels used for boiling H_2SO_4 and the most severely corrosive materials. Other alloys that could be used in the pre-filtration area include Hastalloy C, Incoloy 825, and Inconel 625. The stainless steels and alloys are used primarily before the water removal and particulate removal systems.

Teflon is recommended for out-of-stack heat traced lines. When moisture-laden gases are below the dewpoint, teflon, Carpenter 20 or Hastalloy C, should be used.

Dry sample gas is generally compatible with 316 stainless steel because the corrosivity of the dry gas is low. (See Tables 7 and 9.) Polyethylene and polypropylene are economical choices for dry sample gas maintained above the freezing point without heat tracing. These plastics are not compatible with nitric acid over the long term.

Materials of construction can interact with the sample by catalytic reaction, bulk absorption or surface adsorption. These factors are considered in detail in the section entitled Sample Integrity. No losses by reaction are anticipated for any of the materals listed in Table 7. Absorption and adsorption by the walls of the system must necessarily be transient phenomena since saturation will eventually be reached and, at steady state, the correct concentrations will be measured. Sorption (both absorption and adsorption) by the surface walls will manifest in a slower system response to changes in concentration at the probe tip. Experimental measurements (Figure 5) of system response using sample lines of various materials indicate that adsorption and absorption are negligible for 316 SS, Teflon and polypropylene; are moderate for polyethylene; and are large for Tygon.

Alloys and metals are resistant to abrasion by particulate laden gas streams. Valves, air movers, and probes are subject to abrasion. If heating components fail, water vapor may condense to form an acidic or basic slurry. Components located between the initial and final particulate removers and the primary water vapor removers would be more subject to abrasive effects. High velocity particulate streams tend to remove metallic oxide coatings thereby increasing corrosion potential of some metals.

The heat resistance of various materials is illustrated in Table 12. Typical post control device stack temperatures (Tables 4, 5 and 6) are below the upper temperature limit for Teflon and plastics. Less heat resistant plastics cannot be used in the vicinity of the probe when sampling in the combustion zone.

Sample Integrity

Regardless of the exact design of the sampling interface, it is essential that the sample be transported from stack to analyzer with minimal losses and interactions. There are several mechanisms as mentioned by which interaction

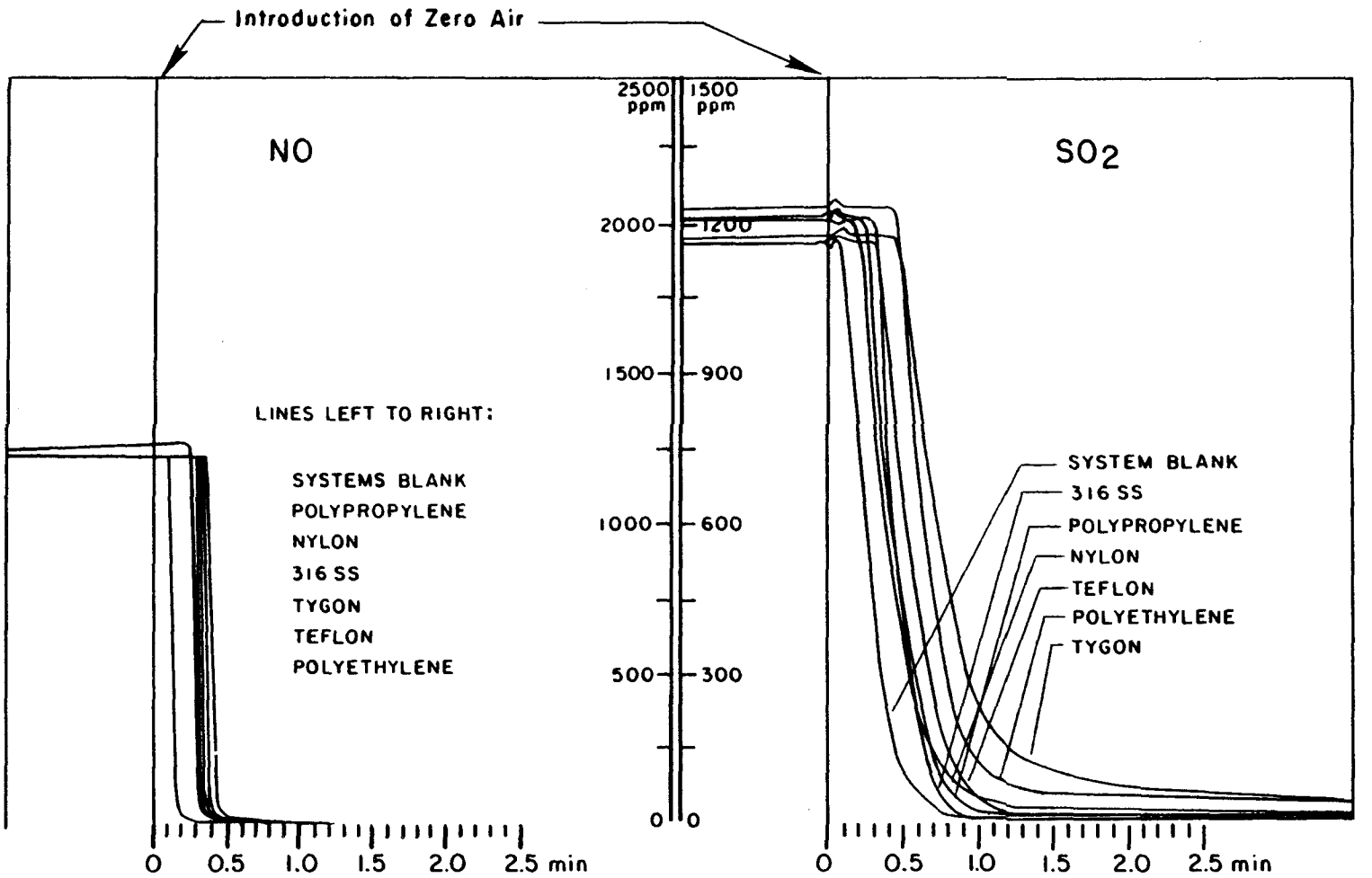

Figure 5. Adsorptive interactions with various sample line materials.[15]

TABLE 12. MAXIMUM CONTINUOUS OPERATING TEMPERATURES FOR CEM MATERIALS OF CONSTRUCTION

Material	Maximum Temp. (°C)
Plastics	
Teflon	250
Viton	150
Polyethylene*	80-125.6
Polypropylene	110
PVC	110
Tygon*	60-82.2
Stainless Steels	
Carpenter 20	871
316 SS	870
304 SS	788
Nickel Alloys	
Hastelloy C-276	1,038
Inconel 625	980
Incoloy 800	760
Incoloy 825	704
Non Metallics	
Aluminum silicate	1,540
Quartz glass (fused silica)	900-1200*
Ceramic	1094-1538*
Zirconium oxide	2,204
Pure Element	
Titanium	800-1000

*Depending on type used.

can occur, including reaction, absorption, adsorption, dilution. Unquantified dilution can occur by air leakage into portions of the system which are under vacuum. Gas phase species can be lost both by homogeneous gas phase reaction and by heterogeneous catalytic reaction on system components or collected particulates.

SECTION 5

MEASUREMENT TECHNIQUES

INORGANIC COMPOUNDS

Inorganic gaseous analyzers can be characterized by detection principles and grouped into the following categories: absorption spectrophotometers, emission analyzers, electroanalytical methods, conductimetric methods, and coulometric methods. Nondispersive infrared (NDIR) techniques can be used for SO_2, NO, CO, and CO_2. Chemiluminescent techniques can measure NO_x. Flame photometric techniques can be used for SO_2. Electrochemical techniques can be used for SO_2, NO_x, HCl, O_2, and CO. Ultraviolet techniques can be used for SO_2 and NO_x. Other techniques such as gas filter correlation and combinations of the above techniques can be used for HCl and CO. Still other techniques such as Fourier transform infrared spectroscopy can measure HCl and various other species.

Nondispersive Infrared Analyzers

Nondispersive Infrared (NDIR) analyzers have been developed to monitor SO_2, NO_x, CO, CO_2, and other gases that absorb in the infrared wavelength region. An NDIR analyzer is basically an instrument that does not disperse the light that is emitted from an infrared source. NDIR instruments utilize a broad band of light that is centered at an absorption peak of the pollutant molecule of interest. This broad band is usually selected from all the light frequencies emitted by the infrared source by using a bandpass filter. Table 13 gives the band centers for several of the gases of interest.

In a typical NDIR analyzer, infrared light from a lamp or glower passes through two gas cells--a reference cell and a sample cell. The reference cell generally contains dry nitrogen gas, which does not absorb light at the wavelength used in the instrument. As the light passes through the sample cell, pollutant molecules absorb a portion of the incident infrared light. As a result, the light emerging from the end of the sample cell will have less energy than when it entered. It also will have less energy than the light emerging from the reference cell. The energy difference is then sensed by a detector, such as a thermistor, a photodetector, a thermocouple, or capacitance arrangement.

A common problem with analyzers that use infrared adsorption detectors is that other gases that absorb in the same spectral region as the pollutant molecule will cause a positive interference in the measurement. For example, water vapor and CO_2 interfere in the measurement of CO. These gases must be removed before the sample gas enters the analyzer. Maintaining a constant

TABLE 13. INFARED BAND CENTERS OF SOME COMMON GASES

Gas	Location of band centers (μm)	Wave number (cm^{-1})
NO	5.0-5.5	1800-2000
NO_2	5.5-20	500-1800
SO_2	8-14	700-1250
H_2O	3.1	1000-1400
	5.0-5.5	1800-2000
	7.1-10	3200
CO	2.3	2200
	4.6	4300
CO_2	2.7	850-1250
	5.2	1900
	8-12	3700
NH_3	10.5	950

moisture level in the sample gas and calibration gas will sometimes calibrate out this effect. A unique solution to this problem is to put the detector cells in series instead of in parallel. The front chamber of the detector absorbs the infrared radiation primarily at the frequencies in the center of an absorption band. Since the front cell takes away energy from the light beam at the center frequencies, the rear measuring chamber will absorb more of the energy in the outer edges of the band than from the center. The geometries and gas concentrations of each measuring chamber are chosen so that the pressure in each remain the same as no pollutant molecules in the sample cell. Once pollutant molecules are introduced into the sample cell, the amount of energy reaching the detector is reduced; however, most of this reduction arises from absorption at the band center, and the front chamber of the detector is affected less by the incoming radiation. The front chamber therefore, is cooler than the rear chamber, causing a pressure difference and a distention of the thin-metal diaphragm. This method is often called negative filtering.

Interfering species generally do not have an absorption band that coincides exactly with that of the species of interest. In such a case, absorption occurs evenly over the region, and the interference is minimized. Several monitors have been constructed utilizing this principle and need less conditioning to remove such species as water and CO_2.

The advantages of the NDIR-type analyzers are relatively low cost and the ability to apply the method to many types of gases. Generally, a separate instrument is required for each gas, although several instruments have interchangeable cells (benches) and filters to provide more versatility.

The disadvantages are that NDIR instruments require more optical maintenance, since large changes in window condition are not automatically compensated for. Also since NDIR instruments are pressure and temperature sensitive, care must be taken to control these parameters. The microphone type detectors are sensitive to vibration and often require both electronic and mechanical damping.

Nondispersive Ultraviolet Analyzers (NDUV) - Differential Absorption

Several available nondispersive systems are based on absorptions in the ultraviolet and visible regions in the spectrum rather than in the infrared. To analyze for SO_2, these instruments utilize one of the narrow absorption bands in the ultraviolet absorption spectrum.

NO_2 may be determined by analysis of its absorption spectrum in the visible region. The instruments designed to operate within these regions are somewhat different from the NDIR methods discussed previously. Essentially, the analyzers measure the degree of absorption at a wavelength in the absorption band of the molecule of interest, 280 nm for SO_2 and 436 nm for NO_2, for example. The major difference is that a reference cell is not used. Instead, a reference wavelength, in a region where SO_2 or NO_2 has minimal absorption, is utilized for signal stabilization and processing. This method of analysis is often termed differential absorption, since measurements are performed at two different wavelengths. This method is not limited to

extractive monitoring systems. It is also used in both in-situ analyzers and remote sensors.

Extractive analyzers using differential absorption have proven to be reliable in monitoring source emissions. Several of the instrument models currently available were designed for in-plant environments. The differential absorption SO_2 analyzers are somewhat more sensitive than the NDIR counterparts. The sequential nature of the NO_x analysis may limit the utility of the method to cases where response times are less important. As with some extractive monitoring systems, particulate matter should be removed before entering the analyzer. It is not necessary, however, to remove water vapor. A heated sample line and heated cell should be used to prevent condensation in the analyzer. Since water does not absorb light in this region of the ultraviolet spectrum, no spectral interferences occur.

Luminescence Analyzers

Luminescence is the emission of light which results from a molecule returning from an elevated energy state to the ground state. Photoluminescence is the release of light after a molecule has been excited by ultraviolet, visible, or infrared radiation. The emission of light from a molecule excited in a chemical reaction is known as chemiluminescence. The atoms of a molecule can be excited to luminescence in a hydrogen flame. These three types of luminescent processes are used in source monitoring applications. Monitors utilizing the principle of luminescence can be specific for given pollutant species and can have greater sensitivity than some of the absorption or electrochemical methods in certain matrices. Monitors that use each of these luminescent processes are discussed in this section.

Fluorescence--

Fluorescence is a photoluminescent process in which light energy of a given wavelength is absorbed and light energy of a different wavelength is emitted. In this process, the molecule that is excited by the light energy typically remains excited for about 10^{-8} to 10^{-4} second. This period of time is sufficient for the molecule to dissipate some of this energy in the form of vibrational and rotational motions. When the remaining energy is reemitted as light, the energy of the light will be lower and light of a longer wavelength (shorter frequency) will be observed. The fluorescence spectrum for SO_2, shown in Figure 6, illustrates this point. Commercially available instruments contain either a continuous or a pulsed ultraviolet light source. The light from the source is filtered to a narrow region that is centered near 210 nm in the near ultraviolet range where the SO_2 molecule will be excited. The fluorescent radiation is measured at right angles to the sample chamber with a photomultiplier tube. Another band pass filter is used to select only a portion of the fluorescent radiation for measurement, since interferences can occur over the range of the fluorescence emission spectrum. Fluorescence monitors have been successfully applied to monitoring source gases as well as ambient air. Using these instruments in source monitoring requires attention to the problem of signal quenching. In the flourescence process,the excited SO_2 molecule may collide with another molecule before it can release its extra energy as light. The energy, instead, will be lost in

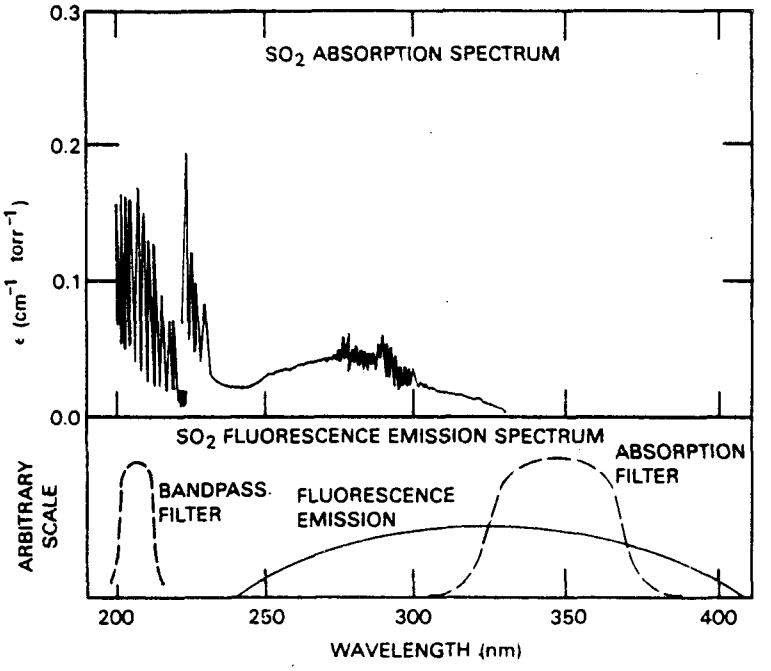

Figure 6. Fluorescence spectrum of SO_2.[9]

the collision and will make the molecules move faster after the collision. Water, CO_2, O_2, N_2, or any other molecule, for that matter, can quench the emission of radiation. Each of these molecules has a different quenching efficiency. If the composition of the background gases in a sample changes by 5 percent O_2 and 10 percent CO_2 in a combustion gas, the SO_2 reading obtained would be different from that obtained if the background gas were ambient air containing 21 percent oxygen. The quenching effect of CO_2 is approximately 50 percent that of oxygen. A decrease of oxygen in a flue gas generally means a relative increase in CO_2. The errors due to the differences range from 5 to 10 percent of the SO_2 concentration. The SO_2 values can be corrected by knowing the CO_2 and oxygen percentages.

Fluorescence monitors, outside of the quenching problem, have few other significant interference problems. Particulates and water must be completely removed from the sampling stream before entering the sampling chamber or the instrument will be easily fouled. Permeation dryers generally are used in these instruments to eliminate any remaining water vapor that is not removed by the extractive system.

Chemiluminescence--

Chemiluminescence is the emission of light energy that results from a chemical reaction. It was found in the late 1960's that the reaction of NO and ozone, O_3, will produce infrared radiation from about 500 to 3000 nm. Figure 7 shows the emission spectrum observed in this reaction. Monitors that measure NO concentrations by observing the chemiluminescent radiation select only a narrow region of the total emission. A filter is used to select light in the region from about 600 to 900 nm. Nitrogen dioxide (NO_2) does not chemiluminesce and must be reduced to NO before it can be measured by this method. Most commercial analyzers contain a coverter that catalytically reduces NO_2 to NO. The NO produced is then reacted with the ozone and the chemiluminescence is measured to give a total NO + NO_2 (NO_x) reading.

Ozone is generated by the ultraviolet irradiation of oxygen in a quartz tube or by spark discharge. The ozone is provided in excess to the reaction chamber to ensure complete reaction and to avoid quenching effects. Since the photomultiplier signal is proportional to the number of NO molecules, not to the NO concentration, the sample flow rate must be carefully controlled. The NO_2 to NO converter chamber is generally made of stainless steel or molybdenum to effect the catalytic decomposition. A few monitors on the market will allow switching the sample gas automatically in and out of the converter to give almost continuous readings for both NO and NO_2.

The chemiluminescence method has been proven reliable and is the most widely used method for source NO/NO_x analysis. Molecules, such as O_2, N_2, and CO_2, quench the light radiation of this chemiluminescent reaction as in the fluorescence measurement technique. The quenching problem has been minimized by (1) choosing a flow rate of ozone into the sample chamber much greater than that of the sample flow rate and (2) using high vacuums to minimize molecular collisions. The ozone dilution gives a relatively constant background gas composition and the effects caused by different quenching efficiencies of different molecules are minimized. The only serious interference is ammonia, which will oxidize to NO in stainless steel converter

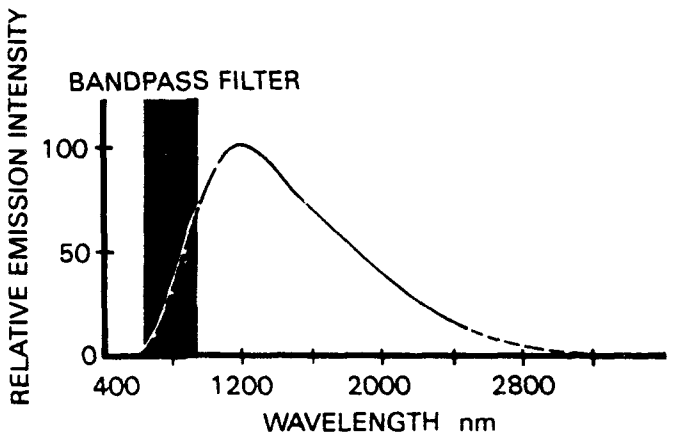

Figure 7. The chemiluminescent emission spectrum of NO_2.[9]

chambers. This is not usually a problem when the monitor is used on a traditional combustion source, however, many hazardous wastes could hydrolyze to form ammonia. Molybdenum converters operated at lower temperatures will not oxidize ammonia.

Photoluminescence (Flame Photometric)--

Another luminescence technique used to detect gaseous pollutants is that of flame photometry. Flame photometric analyzers are primarily used in ambient air sampling, but have been applied to stationary source sampling by using sample dilution techniques.

Flame photometry is a branch of spectrochemical analysis in which a sample is excited to luminescence by introduction into a flame. Instead of using an ultraviolet or visible light source to excite the SO_2 molecule, as in photoluminescence, a hydrogen flame is used to excite the sulfur atom. The excited atom will in turn, emit light in a band of wavelengths centered at about 394 nm, which is then detected by a photomultiplier tube. The method is specific to elemental sulfur, not to sulfur dioxide. Compounds, such as H_2S, SO_3, and mercaptans, will contribute to the ultraviolet emission to give a measure of the total sulfur content of the sample stream. With the use of scrubbers or chromatographic techniques, selective determinations are made for each of these sulfur compounds.

A disadvantage of flame photometric analyzers is the narrow concentration ranges available and the requirement of hydrogen for the flame. Facilities that have strict regulations concerning the use of hydrogen and hydrogen cylinders may find it inconvenient to utilize this method. There are currently only a few manufacturers of source-level flame photometric analyzers capable of detecting sulfur compounds over the expected concentration ranges.

Electronanalytical Methods

Most of the instruments discussed in this report rely on spectroscopic or electro-optical techniques to monitor gases. Another class of instruments based upon electroanalytical methods has found great utility in source monitoring applications. A number of monitors based on polarographic and electrocatalytic methods are available for source monitoring applications. Polarographic analyzers have been developed for a number of gases and can be inexpensive and portable, therefore ideal for inspection work. Complete continuous source-monitoring systems also are available from manufacturers of these instruments. The electrocatalytic or high temperature fuel-cell method, as it is often called, is only used to monitor oxygen. Both extractive and in-stack monitors are available using this technique. The method of conductivity is less widely used and is subject to a number of interferences. Descriptions of this method are given here, since a few instruments employing this principle are still marketed.

The principles behind the polarographic and electrocatalytic methods are somewhat more difficult to understand than the spectroscopic principles discussed earlier. A combination of classical electrochemistry and modern fuel-cell technology has provided the theoretical basis for these developments. An understanding of the underlying operational principles, however, is important for their evaluation.

Polarographic Analyzers--

Polarographic analyzers have been called voltametric analyzers or electrochemical transducers. With the proper choice of electrodes and electrolytes, instruments have been developed utilizing the principles of polargraphy to monitor SO_2, NO_2, CO, O_2, H_2S, and other gases.

The transducer in these instruments is generally a self-contained electrochemical cell in which a chemical reaction takes place involving the pollutant molecule. Two basic techniques are used in the transducer: (1) the utilization of a selective semipermeable membrane that allows the pollutant molecule to diffuse to an electrolytic solution, and (2) the measurement of the current change produced at an electrode by the oxidation or reduction of the dissolved gas at the electrode.

The generation of electrons at the sensing electrode produces an electric current that can be measured. There are two reasons why this type of system may be termed polarographic or voltametric. In typical polarographic analyzers used in chemical laboratories, the electric current in the system is related to the rate of diffusion of the reacting species to the sensing electrode. It turns out that if the rate of which the reactant reaches the sensing electrode is diffusion controlled, the current is directly proportional to the concentration of reactant.

The cells come in a number of configurations, depending upon the manufacturer. Various claims are made about the response and selectivity of the instrument related to the cell design. These systems are small and portable and compared to practically all other source monitoring instruments, are the least expensive. These two factors make them ideal for source inspection, as warning detectors

The polargraphic analyzers in the earlier development stages were temperature sensitive, but temperature compensation devices are now provided to avoid this problem. The cell electrolytes generally are used up in three to six months of continuous use. The cells can be sent back to the company and recharged or new ones can be purchased. It is extremely important that the sample gas be conditioned before entering these analyzers. The stack gas should be at ambient temperature and the particulate matter and water vapor removed to avoid fouling of the cell membrane.

Electrocatalytic Analyzers For Oxygen--

A new method for the determination of oxygen has been developed over the past several years as an outgrowth of fuel-cell technology. These so-called fuel-cell oxygen analyzers are not actually fuel cells, but simply electrolytic concentration cells that use a special solid catalytic electrolyte to aid the flow of electrons. These analyzers are available in both extractive and in-situ (in-stack) configurations. This versatility of design is making them popular for monitoring dilute oxygen concentrations in combustion sources.

In basic electrochemistry, one of the common phenomena studied is the flow of electrons that can result when two solutions of different concentrations are connected together. The electron flow results from the

fact that the chemical potential is different on each side and that equilibrium needs to be reached. The electromotive force (EMF), or output voltage, that results from a concentration cell is described by the Nernst equation.

The instruments designed to continuously monitor oxygen concentrations utilize different concentrations of oxygen gas expressed in terms of partial pressures. A special porous material, zirconium oxide, serves both as an electrolyte and as a high temperature catalyst to produce oxygen ions. A schematic of the electrocatalytic sensing system is shown in Figure 8.

When sampling combustion gases, the partial pressure of the oxygen in the sample side will be lower than the partial pressure of oxygen in the reference side, which is generally that of air. When such a cell is kept at a temperature of about 850°C, oxygen molecules on the reference side will pick up electrons at the electrode-electrolyte interface. The porous ceramic material of ZrO_2 has the special property of high conductivity for oxygen ions. This occurs because the metal ions form a perfect crystal lattice in the material, whereas the oxygen ions do not, resulting in vacancies. Heating the zirconium oxide causes the vacancies and oxygen ions to move about. The oxygen ions migrate to the electrode on the sample side of the cell, release electrons to the electrode, and emerge as oxygen molecules.

A number of manufacturers are presently marketing oxygen analyzers. Both extractive and in-situ type systems have been developed, providing the source operator with versatility in application. A supply of clean air for the reference side of the cell is required. Calibration gases can be injected into the measuring cavity contained within the thimble to check instrument operation.

Paramagnetic Analyzers For Oxygen

Molecules behave in different ways when placed in a magnetic field. This magnetic exhibited behavior is either diamagnetic or paramagnetic. Most materials are paramagnetic; they are attracted by a magnetic field. Paramagnetism arises when a molecule has one or more electrons spinning in the same direction. Most materials will have paired electrons; the same number of electrons spinning counterclockwise as spinning clockwise. Oxygen, however, has two unpaired electrons that spin in the same direction. These two electrons give the oxygen molecule a permanent magnetic moment. When an oxygen molecule is placed near a magnetic field, the molecule is drawn to the field and the magnetic moments of the electrons become aligned with it.

There are three methods of applying the paramagnetic properties of oxygen as a measurement technique in commercial analyzers. These are the magnetic wind or thermomagnetic methods, the magnetodynamic and the magnetopneumatic methods.

Magnetic Wind Instruments (Thermomagnetic)--

The magnetic wind instruments are based on the principle that paramagnetic attraction of the oxygen molecule decreases as the temperature increases. A typical analyzer utilizes a cross-tube wound with filament wire heated to 200°C.

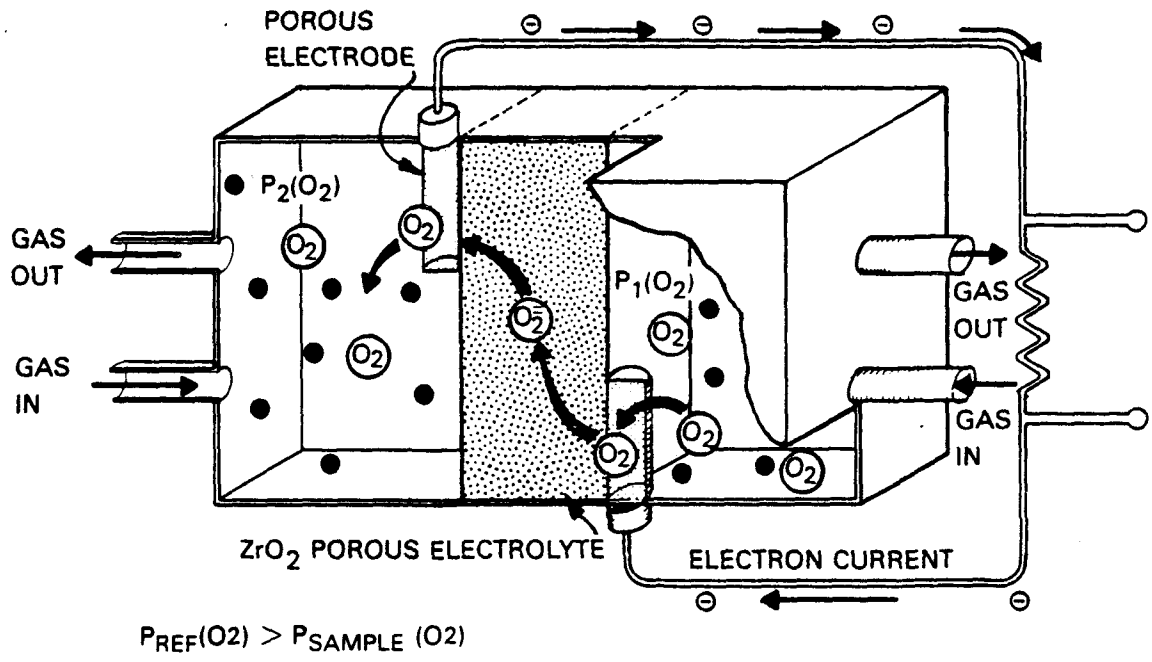

Figure 8. Schematic of an electrocatalytic sampling system.[9]

A strong magnetic field covers one half of the coil. Oxygen contained in the sample gas is attracted to the applied field and enters the cross-tube. The oxygen then heats up and its paramagnetic susceptibility is reduced. This heated oxygen then is pushed out by the colder gas just entering the cross-tube. A wind or flow of gas, therefore, continuously passes through the cross-tube. This gas flow, however, effectively cools the heated filament coil and changes its resistance. The change in resistance detected in the Wheatstone bridge circuit is proportional to the oxygen concentration.

Several problems can arise in the thermomagnetic method. The cross-tube filament temperature can be affected by changes in the thermal conductivity of the carrier gas. The gas composition should be relatively stable if consistent results are desired. Also, unburned hydrocarbons or other combustible materials may react or combust within the heated filaments and change their resistance.

Magneto-Dynamic Instruments--

The magneto-dynamic method utilizes the paramagnetic property of the oxygen molecule by suspending a specially constructed torsion balance in a magnetic field. Here, a dumbbell will be slightly repelled from the magnetic field. When a sample containing oxygen is added, the magnet attracts the oxygen and field lines surrounding the dumbbell are changed. The dumbbell swings to realign itself with the new field. Light reflected from a small mirror placed on the dumbbell is used to indicate the degree of swing of the dumbbell, and hence, the oxygen concentration.

Magnetopneumatic Instruments--

The magnetopneumatic method utilizes the paramagnetic property of the oxygen molecule by introducing oxygen into a disproportional magnetic field. The paramagnetic gaseous substance is attracted to the magnetic field to cause the pressure in that field to rise. The pressure elevation is picked out of the magnetic field by using a nonparamagnetic gas (nitrogen). The electromagnet is alternately magnetized and the pressure change is converted into an electrical signal by a condenser microphone.

All of the commercial paramagnetic analyzers are extractive systems. Water and particulate matter have to be removed before the sample enters the monitoring system. It should be noted that NO and NO_2 are also paramagnetic and may cause some interferences in the monitoring method if high concentrations are present.

Gas Filter Correlation Analyzers

The technique of gas filter correlation (GFC) spectroscopy offers improved specificity over conventional non-dispersive infrared (NDIR) techniques. GFC spectroscopy is based upon comparison of the detailed structure of the infrared absorption spectrum of the measured gas to that of other gases also present in the sample being analyzed. The technique is implemented by using the measured gas itself, in high concentration, as a filter for the infrared radiation transmitted through the analyzer.

The basic components of a GFC spectrometer are shown in Figure 9. Radiation from an IR source is chopped and then passed through a gas filter which alternates between the reference gas and N_2 due to rotation of the filter wheel. The radiation then enters a multiple optical pass sample cell where absorption by the sample gas occurs. The IR radiation exits the sample cell and passes through a narrow band pass interference filter to an IR detector. Gas filter correlation techniques are presently used for continuous measurement of CO and HCl, but could be used for continuous measurement of NO, and SO_2.

Second-Derivative Absorption Analyzers

The second-derivative measurement technique provides a very specific measurement of compounds with narrow band spectral absorption. Light with a modulated wavelength, is projected through the same gas, or measurement cavity. If the gas to be detected is present, the intensity of the detected light varies at twice the modulation frequency. The resulting signal is processed to determine the second derivatives (d^2) value which is directly proportional to the concentration of the gas. Since the technique is sensitive to the curvature of the spectra and not the intensity of the spectra, it provides enhanced sensitivity and permits measurement of a single gas in complex mixtures.

Fourier Transform Infrared Spectroscopy Analyzers (FTS-IR)

Although relatively new on the market for process gas streams, fourier transform infrared spectroscopy can be used for pollution measurements. The FTS-IR uses a rapid scanning interferometer consisting of two mirrors, one movable and one fixed, and a beam splitter. A FTS-IR schematic is shown in Figure 10.

There are no slits, no gratings and no conventional chopper. The mirror is the only moving part in the spectrometer. The beam splitter reflects back 50 percent and transmits 50 percent of the incoming infrared radiation. These two beams are then reflected back towards the beamsplitter by the two mirrors. Depending on the position of the moving mirror, these two beams recombine at the beam splitter with a specific path difference between them. This produces the interferogram. The interferogram is generated by the interferometer modulating the infrared beam as the moving mirror is translated. The modulation frequencies depend on the wavelength of the incident radiation and the velocity of the moving mirror. The interferogram is produced after absorption by a sample, the modulated radiation reaches the detector where intensity is recorded as a function of path difference. The FTS-IR is capable of measurement ranges from the near visible to less than 10 cm^{-1}. FTS-IR systems are compatible with gas chromatograph systems and analysis can be performed in close to real time. Other applications besides quantitative analysis in pollution measurements are spectral subtraction, spectral separation, far infrared analysis, emission spectroscopy and time resolved spectroscopy.

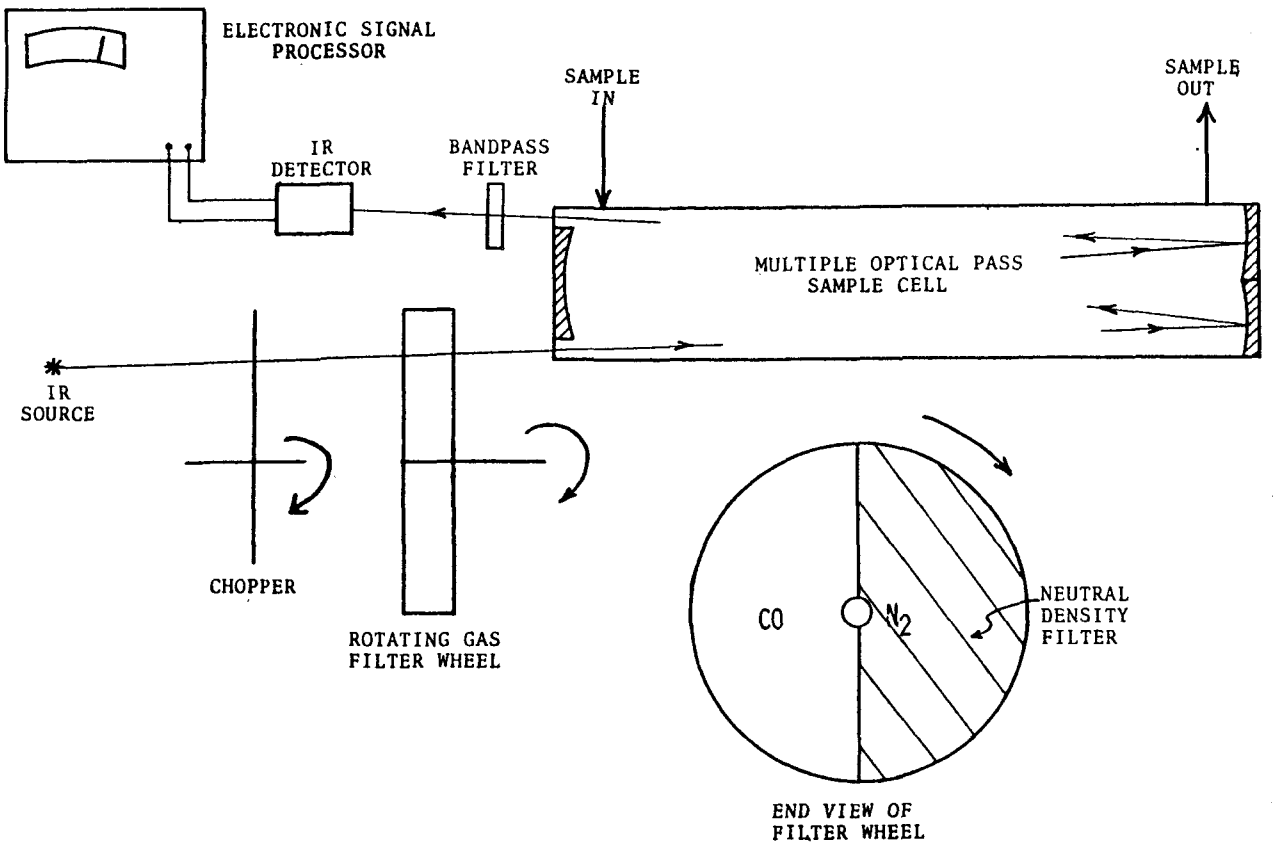

Figure 9. Schematic of a gas filter correlation spectrometer.

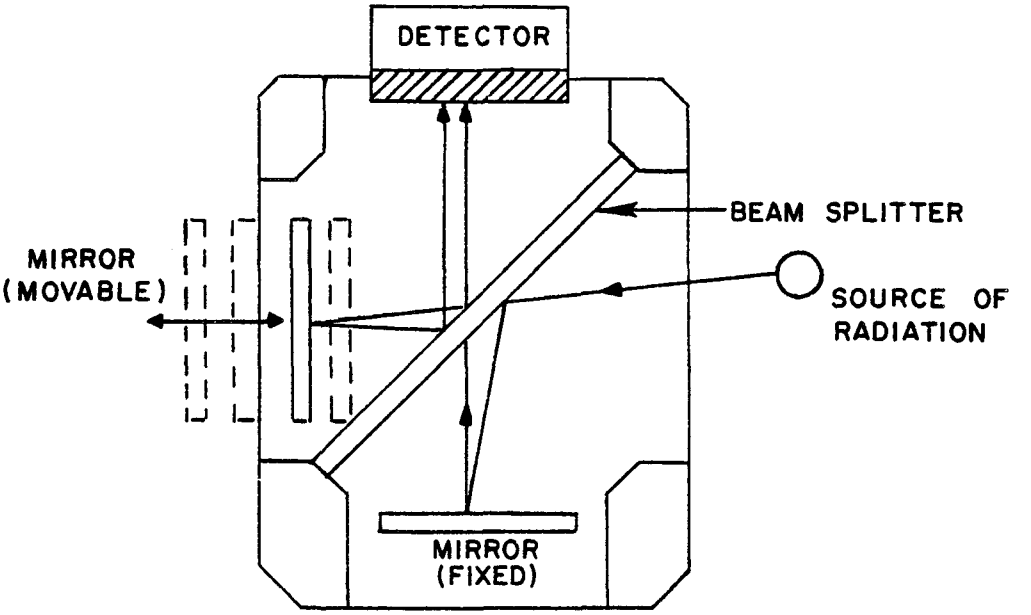

Figure 10. FTS-IR Schematic.

ORGANIC COMPOUNDS

Many varieties of organic species analyzers are available. Gas chromatographic systems include all devices that separate organic species through use of a packed or capillary column and measure the organic concentration using a detector at the end of the column. Several analyzers are hybrid chromatographs, in that, organic/inorganic separation is performed through chemical or thermal techniques and analysis is performed by a typical chromatographic detector, i.e., flame ionization. A third category includes spectrometric systems which bombard compounds with light in the UV, visible or infrared region and measure characteristic absorbtivities and emissivities.

Chromatographic Techniques

Gas chromatography is a common technique used for separating and analyzing mixtures of gases and vapors. A gas mixture is percolated through a column of porous solids or liquid coated solids which selectively retard sample components. A carrier gas is used to bring the discreet bands to a detector and through analysis of the detector response and the component retention time, the sample can be identified and quantified. Gas chromatography has been in use in the laboratory since 1905; however, it has only recently been used in continuous monitoring applications.

Columns--

The column is the heart of the chromatograph in that the choice of the proper column and packing materials is crucial to efficient separation and elution of the components of interest. In some cases, only a capillary tube with a thin liquid coating on the inside wall is used. The most common type of GC column is a liquid coated on an inert solid support contained in a small bore (1/8 in.) stainless steel or glass tube. The choice of the proper liquid coating is crucial and is usually similar in chemical structure to the sample components of interest. Organic compounds can be divided into five classes of solute polarity ranging from most polar (Class I) to nonpolar (Class V). Table 14 lists solute classifications for organic compounds. Compounds having similar boiling points can be separated by choosing column materials of the appropriate polarity. With the right choice, the order of elution of the sample components can be manipulated. Through selection of the best solid support/liquid phase combination, and through optimizing sample size, flow rates, column temperatures and length, and the sensitivity of the detector, a gas chromatograph can be adapted for almost any sample analysis situation.

Since the purpose of a hydrocarbon monitor is to measure concentration of incomplete combustion products of the waste feed material, a chromatographic column and detector must be chosen that is appropriately sensitive to the types of hazardous waste being incinerated and the anticipated partial combustion products. Eighty percent of all hazardous wastes listed in Appendix VIII contain carbon and hydrogen and 28 percent are in the organochlorine compound category. Of the 380 wastes listed, two thirds can be categorized as shown in Table 15. Choosing the correct column components (solid and liquid phases) for an incinerator that burns only one class of compounds is a fairly routine matter and most instrument manufacturers have compiled recommendations based on their experience and their equipment

TABLE 14. SOLUTE CLASSIFICATION

CLASS I (Most Polar)	CLASS II (Polar)
Water	Alcohols
Glycol, glycerol, etc.	Fatty acids
Amino alcohols	Phenols
Hydroxy acids	Primary and secondary amines
Polyphenols	Oximes
Dibasic acids	Nitro compounds with -H atoms
	Nitriles with -H atoms
	NH_3, HF, N_2H_4, HCN

CLASS III (Intermediate)	CLASS IV (Low Polarity)
Ethers	$CHCl_3$
Ketones	CG_2Cl_2
Aldehydes	CH_3CHCl_2
Esters	CH_2CLCH_2Cl
Tertiary amines	$CH_2ClCHCl_2$ etc.
Nitro compounds with no -H atoms	Aromatic hydrocarbons
Nitriles with no -H atoms	Olefinic hydrocarbons

CLASS V (Non-Polar)

Saturated hydrocarbons
CS_2
Mercaptans
Sulfides
Halocarbons not in Class IV such as CCl_4

Source: Ewell, R. N., Harrison, J. M., and Berg, L., Ind. Eng. Chem. 36, 871 (1944).

TABLE 15. APPENDIX VIII CONSTITUENTS ACCORDING TO ORGANIC FAMILIES

Organic family	Appendix VIII (percent)[a]
Aromatic	18
Straight chain paraffins	16
Polynuclear aromatics	8
Nitroso compounds	7
Straight chain olefins	5
Biphenyls	4
Hydrazines	2
Thioureas	2
Ring N aromatic	1
	63

[a]Percent of 300 organic Appendix VIII constituents.

Source: Cudahy, J. J., Sroka, L., and Troxler, W., Incineration Characterization of RCRA listed Hazardous Wastes, July 1981, EPA Report.

restrictions. A commercial hazardous waste incinerator which burns a wide variety of compounds may need to have several columns available. Column switching systems are available with two to four columns installed in a single instrument. Table 16 provides a listing of the types of columns that have been successfully used to analyze certain organic compound classes. Chromatograph columns are available for separation of most types of organic hazardous waste compounds.

An important parameter to consider is response time. A column should be chosen that elutes the compounds of interest first and rather quickly. A shorter column would be preferable over a longer column in order to decrease response time. In commercially available monitors, column lengths vary from 4 inches to several feet (coiled). Shorter columns do not separate compounds as efficiently or as completely as a longer column of the same material. Several short columns of different materials could be arranged to give rapid detection of several compound classes. Backflushing the columns after a designated time can be automated and prevents unwanted compounds from reaching the detectors. The backflush feature is important for compounds like HCl that destroy a sensitive flame ionzation detector.

Detectors--

Once the compounds of interest have been appropriately separated in the column, they are swept into a detector. The following sections describe the available detector types with any limitiations for use with the anticipated hazardous waste streams.

Flame Ionization (FID)--Most organic compounds are pyrolyzed in a hydrogen-air flame. In the FID, the ionic intermediates produced migrate to a detector plate which is appropriately charged. This migration is essentially an electric current which is measurable with sensitive electronic equipment. A chromatographic column is used to separate organic species followed by flame ionization to detect the quantities of carbon and hydrogen in the separated species. The electronic current produced by ionization is proportional to the concentration of the species.

An FID does not respond to the following inorganic compounds:

He	CS_2	NH_3
Ar	COS	CO
Kr	H_2S	CO_2
Ne	SO_2	H_2O
Xe	NO	$SiCl_4$
O_2	N_2O	$SiHCl_3$
N_2	NO_2	SiF_4

Straight chain hydrocarbons produce the greatest FID response. An FID responds differently to different compound classes. Equal amounts of hydrocarbon, esters and ethers do not produce equal FID responses. The sensitivity of an FID is also dependent on the relative flow rates of carrier

TABLE 16. RECOMMENDED COLUMN LIQUID PHASES BY SAMPLE TYPE

Classification of compounds	Stationary phase
ALCOHOLS	
C_1-C_5	Hallcomid M-18 OL
	Carbowax 600 or 1540
C_1-C_{18}	FFAP
	Carbowax 20M
Di-Poly	FFAP
	QF-1
ALDEHYDES	
C_1-C_5	Ethofat
C_5-C_{18}	Carbowax 20M
ALKALOIDS	QF-1
	SE-30
AMINO ACID DERIVATIVES	
N-Butyl trifluoroacetyl esters	DEGS/EGSS-X
BORANES	Apiezon L
ESSENTIAL OILS	
General	FFAP
	Carbowax 20M
ESTERS	
Mixed	Dinonyl phthalate
	Porapak Q
ETHERS	Carbowax 20M
GLYCOLS	Proapak Q
HALOGEN COMPOUNDS	Carbowax 20M
	QF-1 (FS-1265)
	FFAP
Freons	Dibutyl Tetrachlorophthalate
	UCON Polar 2000

(continued)

TABLE 16 (continued)

Classification of compounds	Stationary phase
HYDROCARBONS	
Aliphatic	
C_1-C_5	Propylene Carbonate Carbowax 400 Tributyl phosphate
C_5-C_{10}	Didecylphthalate SE-30
Aromatics	Tetracyanoethylated Pentaerythritol Dibutyl tetrachlorophthalate
Hydroxy	2,4 Xylenyl Phosphate
Olefins	
C_1-C_6	$AgNO_3$/Benzyl cyanide Dimethylsulfolane Propylene Carbonate
C_6-up	Carbowax 20M
Polynuclear	SE-30 on DMCS treated support FFAP on DMCS treated support PMPE (5 ring)
KETONES	Lexan FFAP
NITROGEN COMPOUNDS	
Amines	Dowfax 9N9/KOH
Amides	Versamid 900
Ammonia	Ethofat or Carbowax 600 on Chromosorb T
NITRILES	Tetracyanoethylated pentaerythritol FFAP XF-1150
ORGANO METALLIC	FFAP SE-30
PESTICIDES	Dow 11 QF-1 (FS-1265) SE-30 OV-1 OV-17

(continued)

TABLE 16 (continued)

Classification of compounds	Stationary phase
PHOSPHORUS	SE-30 STAP
SILANES	SF-96 FFAP
STEROIDS	STAP XE-60 QF-1 (FS-1265) SE-30 OV-1 OV-17
SUGAR DERIVATIVES Trimethylsilylethers	QF-1 SE-52
SULFUR COMPOUNDS	Carbowax 20M FFAP Dinonylphthalate Porapak Q

Source: McNair, H. M., and Bonelli, E. J. Basic Gas Chromatography 45, 5th Ed., 1969.

gas, hydrogen and air and upon electrode and linear jet geometry. The FID has the widest linear range of any chromatographic detector in common use, on the order of 10^7, and is sensitive to as little as 2×10^{-11} gm of alkanes.

The major problem with applying this measurement technique is corrosion of the detector plates. HCl gas attacks the stainless steel plates used as grids in the detector and very quickly renders them insensitive. Several manufacturers were contacted to determine if FID detectors were available that would withstand attack by HCl. No detectors were found that were built to withstand HCl gas corrosion, however several manufacturers indicated that detector plates could be built of Hastelloy C-276 or Inconel. The increased cost of highly resistant detector plates should be weighed against the replacement cost of stainless steel detector plates and the costs of additional sample conditioning to remove HCl. At present, an FID will last for several years with routine maintenance at HCl gas levels less than 1000 ppm. Experience on the incinerator ship Vulcanus has shown an FID lifetime of about two weeks at elevated HCl concentrations (8 to 17 percent v/v).[9] Acid resistant detector plates would require only minimal conditioning for HCl since all other GC components are readily available with acid resistant materials such as glass and Teflon.

Electron Capture (ECD)--The electron capture detector measures the loss of electrical signal rather than the produced electrical current. Carrier gas molecules are excited by a radioactive source to produce a steady background current under a fixed applied voltage. When a sample is introduced that absorbs electrons, the current is reduced and this reduction is indicated by an amplifying electrometer. The source of the electron current in an ECD is usually the radioactive decay of nickel 63 or tritium. The high energy electrons emitted interact with the carrier gas which in turn interact with sample constituents. A problem exists when the ionized sample molecules react with other sample constituents to produce an electron which results in confusing detector responses. Usually, a small amount of methane is added to the carrier gas (argon) to deactivate further reactions by excited molecules. However, this dilution of sample gas results in reduced sensitivity. Pure nitrogen carrier gases have been used in laboratory studies with mixed success. The ECD is well adapted for use in the analysis of 10^{-10} to 10^{-12} levels of pollutants incinerator effluents. The detector suffers from the same potential for corrosion as the FID. The ECD may be operated above 350°C if the Ni63 source is used. However it is highly sensitive to temperature changes. Baseline drifts of 50 percent have been reported for a 2°C room temperature change.[11] This detector is extremely sensitive to sub picogram quantities of pesticides, alkyl halides, conjugated carbonyls, nitrides and organometallics, and is quite insensitive to hydrocarbons, alcohols and ketones. Table 17 lists the relative ECD response factors for various organic compound classes. In summary, the ECD is highly sensitive, not very linear, and is very sensitive to surrounding conditions, therefore probably not well suited to the rigorous demands of continuous monitoring.

Photoionization (PID)--The photoionization detector is similar in principle to an FID and ECD except that an energy source in the UV-visible wavelength region is used. Many inorganic species form ions upon exposure to UV radiation, some organic species requiring higher UV energy levels to ionize

TABLE 17. ELECTRON CAPTURE DETECTOR RELATIVE RESPONSE FACTORS (BENZENE = 1)

Factor	Compound or class
<1	Aliphatic hydrocarbons
1-10	Aromatic hydrocarbons Alcohols, ketones, ethers Monofluoro compounds
10-100	Amines, esters, aldehydes, nitriles Monochloro compounds Trifluoro compounds
$100-10^3$	Dichloro aliphatic compounds (some) Stilbenes Oxalates
10^3-10^4	Dichloro aliphatic compounds (some) Monobromo compounds Hexafluoro compounds
10^4-10^6	Dichloro aromatic compounds Mononitro compounds
10^9	Monoido compounds Dibromo compounds Trichloro (or greater) compounds

Source: American Laboratory, Electron Capture Detectors and their applications to Toxicology.

than others. Formaldehyde, acetonitrile, chloroform, and carbon tetrachloride are some of the organic species that are difficult to photoionize. Some inorganic gases that are difficult to photoionize include hydrogen sulfide, chlorine, and oxygen. Using the appropriate column with the appropriate energy level UV lamp allows characterization of compound classes. Available lamp energies range from 8 to 12 eV. The lower lamp energies provide increased selectivity for polyaromatic compounds while the higher energy lamp is more sensitive to aliphatic and olefinic organics. In order to identify a variety of organic species in a given sample, three to five separate lamps would be required along with a computer to quickly interpret the relative responses. PID detectors are also available that do not use chromatographic columns. Even in combination with a column, a single PID instrument would have limited uses at a facility burning a wide variety of compounds. These detectors are typically specified for applications where the sample matrix is well characterized since the PID responds to both inorganic and organic species.

Advantages of the PID include sensitivities equal to or greater than an FID (10 to 50 times for certain organic compounds) and the fact that the sample is not destroyed. The PID is available with all parts contacting the sample, except the light window (quartz), coated with Teflon. Disadvantages include reduced sensitivity from dust or coatings on the sample cell windows and the need for several instruments or differing lamp energies to identify and detect a complex mixture of organic species.

Other Detectors--The previously mentioned detectors - FID, ECD and PID, are the most commonly used chromatographic detectors for air pollutant analysis. The thermal conductivity detector (TCD) is a common detector that is sensitive to all compounds. Since pollutants at trace levels are of interest in hazardous waste incinerators, the other components of the sample would pose an insurmountable selectivity problem with this analyzer. Highly selective detectors have been developed where sensitivity to certain compounds or elements in compounds has been enhanced. Alkali Flame Ionization Detectors (AFID) were developed to analyze pesticides. With the AFID, a small pellet of Cs, Br, or Rb_2SO_4 is placed at the tip of a typical FID burner which is operated in a starved oxygen mode. The sensitivity of the detector to phosphorous containing compounds is enhanced 5000 to 1 over normal hydrocarbons. Different salt pellets have been used to enhance sensitivity to different elements, the next most common application being nitrogen compounds. The Hall Electrolytic Conductivity Detector (HECD) is particularly sensitive to nitrogen, sulfur and halogen containing compounds and is more discriminating than the ECD. The Thermionic Specific Detector (TSD) is also a highly sensitive detector that is specific for nitrogen containing compounds. These detectors usually achieve selectivity and sensitivity at the expense of durability and reliability. Many of the more recent noncontinuous EPA sampling and analysis methods recommend the use of these detectors. The durability and reliability of these detectors may be improved to the point where continuous monitoring applications would be feasible.

Several of the EPA methods also recommend using mass spectrometry (MS) in combination with a GC. A mass spectrometer is a powerful instrument capable of identifying compounds and structures. GC/MS and other

instrument/instrument combinations such as GC/IR and FTIR/GC are presently in use in the laboratory environment. GC/MS has been used in mobile monitoring efforts, however, no continuous monitors per se were found to be in current use. Mass spectrometers are finding some use in process monitoring in certain applications, however not enough data is available to reasonably assess the adaptability of these instruments and combinations of instruments to continuous monitoring of incinerator effluents.

Dual Detectors--Combining the high sensitivity of the FID detector to easily pyrolized, low boiling organic compounds with the high sensitivity of ECD detectors to higher boiling aromatics, etc., is one method for more complete quantification of organic emissions from an incinerator. One instrument could be chosen with two columns, each specified to enhance the separation of and response time associated with the appropriate organic compounds. One or both detector(s) could be used at a given time, depending on the waste being burned. The nondestructive nature of the PID detector allows its use in series with other GC detectors. PID/FID, PID/ECD and PID/NPD combinations have all been used for specific applications. A typical PID/FID application is the identification of hydrocarbon classes. The PID response increases with increasing degrees of unsaturation and the FID response is mostly unaffected by double bonds. By comparison of the relative response of these two detectors, alkanes, olefins and aromatic compound classes can be identified in complex sample matrices.

Hybrid Chromatographs

A basic gas chromatograph consists of a series of sample separation and detection equipment as discussed previously. Many combinations of these basic components are possible which would allow virtually any organic compound to be identified. Numerous columns can be used in parallel or in series to tailor the sample separation and retention time to a particular need. Various detectors could be used in parallel or in series to enhance sensitivity and selectivity to compounds of interest. Since gas chromatography involves both a separation and detection step, in some cases only one of these steps may be needed. A variety of other instrumental methods; GC/MS, GC/IR and GC/FTS-IR combines a chromatographic separation with an instrumental identification of the components of the eluted materials. The combination of a GC and other instrumentation results in more of a research oriented monitor and the capital costs are orders of magnitude higher than the simple GC.

Many commercially available organic species analyzers are comprised of a sample alteration system and an FID detector. Organic species may be reduced to methane, water, or CO_2 which is then analyzed. Many other instruments consist of only an FID detector with no chromatograph or other sample treatment. Combining these two instruments provides a method for determining methane and nonmethane hydrocarbons simultaneously. One sample is passed directly into the flame to determine total hydrocarbons while a second sample is passed through a stripper column to remove everything except methane and by difference, the nonmethane hydrocarbons can be quantified. Using a selective combustor instead of a stripper column provides an indication of total reactive hydrocarbons. Depending on the operating temperature of the combustor, one can convert olefinic (250 to 500°C) or paraffinic (to 1000°C)

compounds to water and/or methane and by difference between total and reacted detector responses, one can determine the methane concentration. With proper sample conditioning, these dual response instruments may be well suited to order of magnitude analysis of incinerator effluents.

GC/IR--

Combining the separation and detection power of a GC with the identification capabilities of an IR absorption spectrometer produces a more specific instrumental technique for identification of organic compounds. To date, the major problem with combining these techniques has been the development of suitable equipment to interface the two instruments. The volume of sample from the GC is traditionally only a tiny fraction of the volume of sample usually required by an IR instrument. Reducing the cell volume of the IR decreases sensitivity unless additional passes through the cell are provided. IR cells (light pipes) have been developed that are compatible with capillary GC instruments and through the development of computer software, GC/IR and GC/FTS-IR are gaining popularity as the "poor mans" GC/MS. Within the next few years, this technology will be developed to the point where it will be applicable to continuous air pollutant monitoring. At present, only 55 toxic substances have been detected in the laboratory with the GC/FTS-IR technique with minimum detectable quantities on the order of 1 to 10 micrograms.[12]

GC/MS--

A compound in a gas matrix can be more fully identified through analysis of retention time in a GC and the mass spectrum. Identity can be established by comparing the total ion current profile of an eluted compound to a published standard spectrum. GC/MS techniques are particularly suited for analysis of organics in water through a concentration step. GC/MS has been used to identify organic ambient air contaminants. The concentration step involves passing the air sample through an absorber column that traps the organic material followed by thermal or solvent desorption of that material into the GC. This technique is semicontinuous and overall response times of a GC/MS are typically greater than 3 minutes. This powerful research tool could be adapted to identify and quantitate organic compounds in incinerator effluents in close to real time. At present, no GC/MS instrumentation is in routine use as a continuous monitor. Double mass spectrometry (MS/MS) and laser multiphoton ionization mass spectrometry have been identified as potential on-line or real time instruments for the identification of polycyclic aromatic hydrocarbons.[13] These instruments do not use the GC for separation of components and therefore do not involve the same delays in response time.

A disadvantage of GC/MS and MS/MS techniques is the complexity and cost of the instrumentation. Investments costing more than $75,000 are usually required. The mass spectra produced is complex and close to real time results can only be provided through a computer with extensive library searching capabilities. The MS can scan for certain compounds within seconds; however, full spectrum scans usually take greater than 3 minutes. These disadvantages should be weighed against the high sensitivity and resolution capabilities of the GC/MS system.

Radiation Emission/Absorption Instrumentation

All organic compounds absorb electromagnetic radiation because all contain valence electrons that can be excited to higher energy levels. Absorption measurements in the visible and ultraviolet wavelength regions are useful for detecting the presence of certain functional groups that contain valence electrons with relatively low excitation energies. Absorption measurements in the infrared wavelength regions are useful for identifying specific compounds since no two organic compounds (except for optical isomers) have identical infrared absorption curves. The applicability of absorption measurements to characterize incinerator effluents involves the choice of the appropriate energies and wavelength.

A given compound normally exhibits one or two maximum absorption peaks in the UV and visible region and may have numerous maximum and minimum absorptivities in the IR region. Aromatic hydrocarbons absorb strongly in the near ultraviolet region, however, aliphatic hydrocarbons absorb in the region of 3 microns. Ideally, measurements are made at several wavelengths where the substances of interest absorb while other components do not. Since all compounds absorb radiation, these methods suffer from a lack of specificity. Through chemical alterations and substitutions, one can identify several compounds in a sample; however, this laboratory procedure has not been demonstrated on a real time basis for more than one compound (phenol). Absorption or emission in the X-ray region of the spectrum will not be considered here since the instrumentation has not yet been applied in a continuous emissions monitoring situation.

Radiation absorption instrumentation consists of a radiant source, a wavelength control system, the sample chamber, a signal detector, and an indicator. Various types of lamps are used; from a common tungsten filament light bulb to a CO_2 laser depending on the wavelength region of interest and power requirements. Wavelength selection is accomplished most cheaply with absorption and interference filters where a short wavelength range is transmitted. A monochrometer can resolve radiation into its component wavelength through use of a system of slits and lenses, prisms and/or diffraction gratings. Sample compartments or cells must be constructed of materials that pass radiation in the spectral region of interest with minimal interference. Radiation detection and indication is usually accomplished through use of photovoltaic cells, photomultiplier tubes, or photoconductive cells. Digital, dial, and other indicators are used to provide the quantitative results.

The following sections describe the principles of various absorption/emission measurements related to organic compounds, the compounds for which the method is selective and any advantages and/or limitations to using the instruments at the three incinerator sampling locations of interest.

Infrared Absorption--

The infrared portion (IR) of the spectrum ranges from wavelengths of 2.4 to 14 microns and the near infrared (NIR) ranges from 1 to 2.5 microns. Most organic species absorb radiation in the IR region and the concentration of species can be determined by the nature of the transmitted radiation. The

concentration of an absorbing compound is inversely proportional to the sample cell path length and proportional to the energy transmitted through the sample divided by the logarithm of the energy entering the sample (Beers law). Sensitivity can be increased through increasing the cell path length and by including multiple radiation passes through the sample. High radiation energy sources such as CO_2 lasers are finding increased use.[14]

The near infrared region has found increasing application to process and pollution monitoring for several reasons. Sample cell window and lens materials have been developed which are physically more suitable for extra-laboratory use. Radiation source energies and detector sensitivities are also correspondingly higher. The most common radiation source is an inert heated solid material, commonly known as a black body generator. The Nernst glower, composed of rare earth oxides or the Globar, composed of a silicon carbide rod, are typical commercial IR sources. A typical NIR source consists of a quartz diode lamp.

Determining the appropriate wavelength to monitor will depend on the organic species of interest. General IR absorption characteristics of classes of compounds are given in Table 18. Scanning the 6 to 9 micron (1665 to 1110 cm^{-1}) wavelength region would allow for detection of most types of organic compounds. To identify individual compounds in a complex mixture with IR is complicated by overlapping absorption bands and shifts in characteristic wavelengths. Computerized compound identification, where large numbers of IR spectra are stored and rapidly compared with the spectra at hand, may allow almost real time identification of simple sample matrixes. The use of computers with IR instrumentation is primarily a laboratory function and not yet useful as a continuous monitoring tool.

Presently, most continuous monitoring instruments measure absorption at only one or two wavelengths. In-situ IR instruments are available but are not considered applicable to monitoring a hazardous waste incinerator. Extractive IR instrumentation have advantages and disadvantages depending on the system design. Instruments that utilize one and two IR sources and a separated reference and sample cell suffer from drift caused by particulate in the sample. Instruments using a single cell use mirrors to increase the path length which require maintenance and in many cases, careful adjustments.

Ultraviolet--

Aromatic hydrocarbons absorb radiation in the near ultraviolet wavelength region. Aliphatic hydrocarbons typically do not absorb in this region to any great degree. Compounds can absorb over both wide and narrow wavelength bands and continuously absorb over several discrete bands. By determining the absorption maxima, wavelength, and absorption intensity one can identify an organic chromophore (e.g., a carbonyl group). Wavelength shifts can be attributed to the presence of double and triple bonded species and rules have been developed to aid in the identification of these species. There are many variables and interferences involved with UV absorption measurements since inorganic species also absorb at these wavelengths. Absorption is affected by pH and nonabsorbing species that can react with solvents and numerous other reagents to form absorbing species. Differentiating organic from inorganic species and separating overlapping spectral bands can be done through use of

TABLE 18. IR CHARACTERISTIC WAVELENGTHS

Compound class	Band of interest (stretch, wag, rotation)	Wavelengths m (cm^{-1})
Aromatic Hydrocarbons	C-H stretch	3.2-3.3 (3125-3039)
	C-C stretch	6-7 (1665-1430)
Aromatic Halogenated Hydrocarbons	C-F[a] stretch	8 (1250)
	CH_2-Cl wag	8 (1250)
Aromatic Ether	C-O vibration	8.5-9 (1175-1110)
Aromatic Ketones	C-O stretch	6-6.2 (1665-1615)
Aromatic Alcohols and Phenols	O-H stretch	2.7-3.2 (3705-3125)
	C-O stretch	7.5-8.5 (1335-1165)
Aromatic Amines	N-H stretch	2.9 (3450)
	C-C stretch	6.2 (1665)
Nonaromatic Amines	N-H stretch	3 (3335)
	N-H deformation	6.2 (1615)
Nonaromatic Aldehydes	C-O stretch	5.9-6 (1695-1665)
Nonaromatic Ketones	C-O, C-C stretch	5-6.7 (2000-1495)

(continued)

TABLE 18 (continued)

Compound class	Band of interest (stretch, wag, rotation)	Wavelengths m (cm^{-1})
Nonaromatic Alcohols	C-O stretch	8-10 (1250-1000)
Nonaromatic Hydrocarbons	C-H stretch	3.4-3.5 (2940-2855)
	C-H bend	6.8 (1470)
Nonaromatic Halogenated Hydrocarbons	C-F stretch	15 (665)
	CH_2 deformation	8 (1250)

[a]F = halogen, Cl, Br, etc.

Source: The Aldrich Library of Infrared Spectra, Second Edition, 1975 by Charles J. Pouchart

derivative UV absorption spectroscopy. Here, selectivity is improved by modulating the incident wavelengths and detecting the second harmonic of the emitted modulation frequency. This method is preferred over simple UV spectroscopy since the results are not influenced significantly by sample opacity, light intensity fluctuations or the presence of particulate matter in the sample. Instrumentation is presently available that can scan several wavelengths in a few seconds and in effect provide a real time analysis.

Aromatic compounds all have a very strong absorption peak at 184 nm. Identification of each aromatic compound usually requires analysis of the weaker absorption bands. Table 19 provides a listing of the next two wavelengths where weak absorption occurs for several aromatic compounds. An instrument capable of scanning 180 to 320 nm may allow identification of these compounds.

TABLE 19. UV ABSORPTION WAVELENGTHS OF AROMATIC COMPOUNDS

Compound		Weak band λ_{max} (nm)	Weaker band λ_{max} (nm)
Benzene	C_6H_6	204	256
Toluene	$C_6H_5CH_3$	207	261
m-Xylene	$C_6H_4(CH_3)_2$	-	263
Chlorobenzene	C_6H_5Cl	210	265
Phenol	C_6H_5OH	211	270
Phenolate ion	C_6H_5O-	235	287
Aniline	$C_6N_5NH_2$	239	279
Anilinium ion	$C_6H_5NH_3$	203	254
Thiophenol	C_6H_5SH	236	269
Naphthalene	$C_{10}H_8$	286	312
Styrene	$C_6H_5CH{=}CH_2$	244	282

Other Radiation Methods--

The intrumental measurement of absorbtivities in the UV and IR wavelength regions discussed previously was based on first order absorption. Derivative or wavelength modulated derivative spectroscopy is a technique where the incident wavelengths are modulated by a few nanometers and the absorbed second haromonic of this frequency is detected. Basically, instead of determining peak absorption wavelengths, the curvature of the absorption peak is also measured. Measurement of this curvature provides increased selectivity. A prototype derivative UV absorption spectrometer (DUVAS) has recently been field tested and appears to be a promising continuous montioring tool. These instruments require computer controllers and can scan a 100 nm wavelength range within minutes. As additional derivative absorption spectrums are developed and stored in computer memories, more and more complex samples can be quickly identified.

Polycyclic organic materials are inherently fluorescent and the use of laser-induced fluorescence has been determined to be a potential real time monitoring tool.[15] This technique requires a separation step to be selective and through use of a tuneable laser, problems with band overlapping and broadening could be overcome. There is little to no data on the fluorescent spectra of aromatic compounds and no commercial continuous monitoring instruments were found.

Total luminescence spectroscopy is a technique where excitation and emission wavelengths are compared to identify a compound. This technique is applicable to identification of a single compound in a noninterfering background and is not applicable to the determination of components of a mixture. Polynuclear hydrocarbons in hexane have been identified at ppm levels with this technique however no continuous monitoring instrumentation appear to be available.

DATA ACQUISITION AND CONTROLS

The development of a continuous emissions monitoring system goes beyond the gas analyzers and conditioning system. The analyzers must measure emissions within specified time periods. The measurements then must be recorded in some manner. After the data are recorded, these must be converted into units of the emissions standard.

Presently, after a permit is issued, incinerator operators must continuously monitor temperature, waste feed rate, air flow rate and stack gas carbon monoxide levels. Incinerators operating in interim status are required to monitor any existing instruments which relate to combustion and emission control at 15 minute intervals.

A complete emission monitoring system, therefore requires some means of recording the analyzer data. Strip-chart recorders have been used most often, but data loggers and computer systems are beginning to become more popular. Data processers have been developed specifically to reduce the time necessary to evaluate and report emissions.

A data reporting system may encompass anything from manual resolution of raw strip chart data and compilation of associated data to the near fully automatic preparation of complete emission reports. The choice of the data reduction and reporting system may be the most important factor in the overall continuous emission monitoring system.

The control/data systems can be tailored to yield a complete printed report. The user has the advantage of implementing digital processing automation to whatever extent desired contingent upon economic and technical constraints. Multiple stacks or duct locations can be accomodated with hourly, daily and weekly reports with standard data processing hardware and software. The addition of reason codes generally requires the addition of a hard disc. While the standard software supports reports on a weekly basis, a larger storage capability allows custom software to support data for a calendar quarter, or longer. The cost of such a system is largely dependent upon the features requested.

SECTION 6

EVALUATION OF COMMERCIALLY AVAILABLE EQUIPMENT

Presently available continuous emission monitors utilize a wide range of techniques for determination of pollutant emission rates. Evaluating the usefulness or the adaptability of these instruments to monitoring in three zones of an incinerator involves numerous considerations. The monitor and conditioning system must operate with minimum maintenance requirements and be reliable enough to be linked to automatic shutdown systems. The conditioning system must provide a sample in close to real time and the analyzer should respond within seconds. In the following sections, the available equipment will be summarized by outlining advantages and disadvantages based on the above considerations.

INORGANIC MONITORS

Specifically this program involved an assessment of continuous source monitors. Manufacturers were contacted to obtain information on their respective analyzers and commercial products required in their sampling systems. This information was then used as a basis for the sampling system requirements for each analytical technique.

The design of an adequate inorganic extractive interface for continuous monitoring of SO_x, NO_x, CO, CO_2, O_2, and HCl from hazardous waste incinerator sources involves a number of engineering choices and tradeoffs. An "adequate" or a "minimum" sampling interface is the simplest and least expensive system that will permit continuous monitoring within certain specified tolerance limits.

The design of a sampling interface must be predicated on the specific source/analyzer combination for which it is intended. Typical source characteristics were given for hazardous waste incinerators. Sample conditioning requirements are given for nine types of commercially available analyzers including NDIR, UV (differential absorption), luminescence, electroanalytical, conductimetric, coulometric, colorimetric, thermal conductivity, and specialized IR. Although it is difficult, in the absence of field test data, to recommend a specific system which will achieve the aforementioned criteria, a minimum assessment is presented.

Most analyzers are sensitive to pressure and must be controlled at a fixed pressure value by venting to atmosphere. Sample flow rate is not a critical parameter and the need for flow control devices or back pressure regulators is not anticipated. A flow rate on the order of 1 SLPM is typical of analyzers surveyed. Sample temperature is not a critical parameter as long

as it remains within fairly wide limits. All analyzers which are sensitive to sample temperatures provide internal control. The sample pump must be positioned upstream of the analyzer if pressure is controlled by venting to atmosphere.

The proper choice of materials of construction is an important part of the interface design. Information has been presented on chemical resistance and heat resistance. The stainless steel and nickel alloys are somewhat versatile but limited in corrosive atmospheres and the chemically inert materials such as glass, ceramics, and refractory metals are extremely heat resistant but fragile. Plastics and fluoroplastics are extremely good in corrosive atmospheres but have limited heat resistance.

For incinerator sources, coarse filtration is required before the sample is withdrawn from the stack. A few types of filters have been mentioned: (1) the "external" or exposed filter in which the filter element is supported within the duct or stack, and (2) the internal or in line filter which is also supported within the stack or duct but is exposed only to the withdrawn sample. The internal arrangement is recommended when calibration gases are to be injected at the probe tip. Calibration of the analyzers can be accomplished by using simple timing devices to actuate solenoid valves.

Sample line materials can be plastics or fluoroplastics except for the first few meters in the vicinity of the stack or duct when sampling in the combustion zone. Heated sample lines can be used to keep the sample above the dewpoint. The tolerance limit or system response time can be easily met without extracting excess sample and bypassing the excess to vent. Dead end volumes have little effect on system response time but large mixing volumes can have a significant effect. When pressure is controlled by venting to atmosphere, the most suitable type of sampling pump is the diaphragm pump. Other types of air movers have been discussed, such as eductors and ejectors, but should be used when dilution is necessary and moisture is not removed from the system.

Moisture removal is an important part of the interface design. Only NDIR instruments require the maintenance of a constant moisture level. Moisture can be removed by condensation, permeation distillation and membrane separation or not removed at all by maintaining the sample above its dewpoint or by sampling using air dilution.

Fine filtration is accomplished either in the conditioning system or internally in the analyzer itself. Useful control measurements for the conditioning system include the sample flow rate, the pump suction and discharge pressures, and sample line temperatures.

The exact nature of hazardous waste incinerator exhaust gases depends to some extent on the type of emission control process that is used. If a dry-absorption process is used to reduce emissions, moisture removal components are less necessary, however, acid mist must be removed. If a wet scrubber is used to control emissions, acid mist removal is accomplished but water vapor must be removed or controlled at a fixed level for NDIR instruments. The basic conditioning system components for sampling dry stack

gases are probe tip filter, acid mist remover, sample pump, and fine filter. The basic components for sampling wet stack gases are probe tip filter if required, sample pump, moisture removal or dropout system, and fine filter. If large volumes of NO_2 are present heat tracing should be used to keep the sample above its dewpoint or a permeation dryer can be used to selectively remove water vapor while retaining other gases. Heat tracing as the only control measure for high moisture contents is not recommended for NDIR instruments which are sensitive to water vapor. Heat tracing may be unacceptable for chemiluminescent and electroanalytical analyses if the dewpoint is above their maximum allowable sample temperature. Heat tracing as the only control is a viable alternative for all other instruments. Permeation drying can be used with all instruments and can represent a cost savings over heat tracing. The same additional interface components are required.

The distinguishing disadvantage of NDIR analyzers is their sensitivity to water vapor. This requires either moisture removal to below 3 percent or maintenance of a constant moisture level in both the sample and calibration gases. Many flue gas constituents have overlapping absorption wavelength bands and it is difficult to isolate an absorption wavelength band for a specific constituent that is not influenced by other constituents of the stack gas. The main advantage of NDIR analyzers in continuous measurement is that it is less expensive than comparable UV analyzers. It also is the best way to analyze combustion control parameters (CO and CO_2).

An advantage of UV analyzers is high operating temperature capabilities. Most manufacturers recommend that the sample be kept above the dewpoint. UV analyzers are tolerant to limited amounts of particulates. If sufficient particulate removal is obtained in coarse filtration, fine filtration is not required.

There are no particularly noteworthy aspects of electroanalytical analyzers except for removal of interferences and low price.

The chemiluminescent analyzers must have some means, internal to the instrument itself, to control the flowrate of the sample to the reaction chamber. Some manufacturers control internal flow and pressure with regulators. Some analyzers draw sample through the analyzer using a pump on the downstream side. Moisture can be removed in chemiluminescent analyzers by a room temperature trap provided the analyzer is kept above room temperature. The main advantage of the chemiluminescent technique is sensitivity and broad concentration ranges measurable with one instrument.

Other luminescent techniques, such as flame photometric detection and fluorescence have advantages in that they are specific to sulfur compounds. A disadvantage is that, when applied to flue gas measurement, dilution is required from 1,000-10,000 to 1 so that the detector can operate in its optimum range.

Other analytical techniques include gas filter correlation and Fourier transform infrared which could be applied to continuous measurement of HCl and a combination colorimetric/photometric analyzer for SO_3 measurement. These

techniques cannot be assessed on a continuous basis on hazardous waste incinerators without a proper field evaluation.

One of two problems faced with implementing an interface design is locating manufacturers of suitable components. A number of components are fabricated cheaply, but in many cases the cost of labor for fabrication makes it less expensive to buy commercially available components.

In conclusion, sample conditioning development for source sampling is in a state of flux. Each manufacturer seems to have his own idea as to what configuration a sample conditioning unit should take. Well designed, reliable sample conditioning systems can cost as much or more than the analyzers attached to it. It must be remembered that no matter how good the analyzer is, no analyzer will work properly with poor sample conditioning.

Sample conditioning systems have been and are being presented to industry in a variety of forms. One such system consists of a probe, heated sample line, water trap, and aspirator. There are pressure-type systems which utilize a probe, heated sample line, heated pump, heated filters, and refrigerated water trap. There are systems that only utilize a filter at the probe, and others that use heated probes with external filters.

In short, presently available commercial conditioning systems are not fabricated to handle typical incinerator conditions but specialized fabricated systems can be developed by the vendors to fit the particular application.

ORGANIC SPECIES MONITORS

Presently available organic species continuous monitors can be divided into two basic types, instruments that can detect a large number of compounds and instruments that detect only one or two compounds. A commercial hazardous waste incinerator burning a wide variety of wastes would likely need an instrument capable of detecting at least four organic compounds or compound classes. The capital costs of these two general types of equipment are not appreciably different. If further regulatory demands include continuous compliance monitoring of more than one organic component, instruments that convert organic compounds to CO_2 or CH_4, followed by detection of these species, may not be applicable. Single or double wavelength spectrometers and methane monitors would be of little use compared to spectrometers that scan a wavelength range or chromatographs that also detect a variety of compounds.

Most presently available monitors offer ppm levels of sensitivity whereas an incinerator effluent typically contains parts per billion or parts per trillion levels assuming that 99.998 percent or greater DRE is maintained. Instruments that offer sensitivity at these low ranges are presently laboratory type instruments that are not yet field proven for continuous monitoring applications. DRE field tests are performed by concentrating the sample prior to analysis in order to provide sufficient sensitivity. The dynamic ranges of typical organic laboratory instrumentation is provided in Figure 11. The ranges of continuous emission monitors using these detection techniques would be similar. Data on the long-term use of continuous sample concentrating equipment, such as that sometimes used as an interface between a

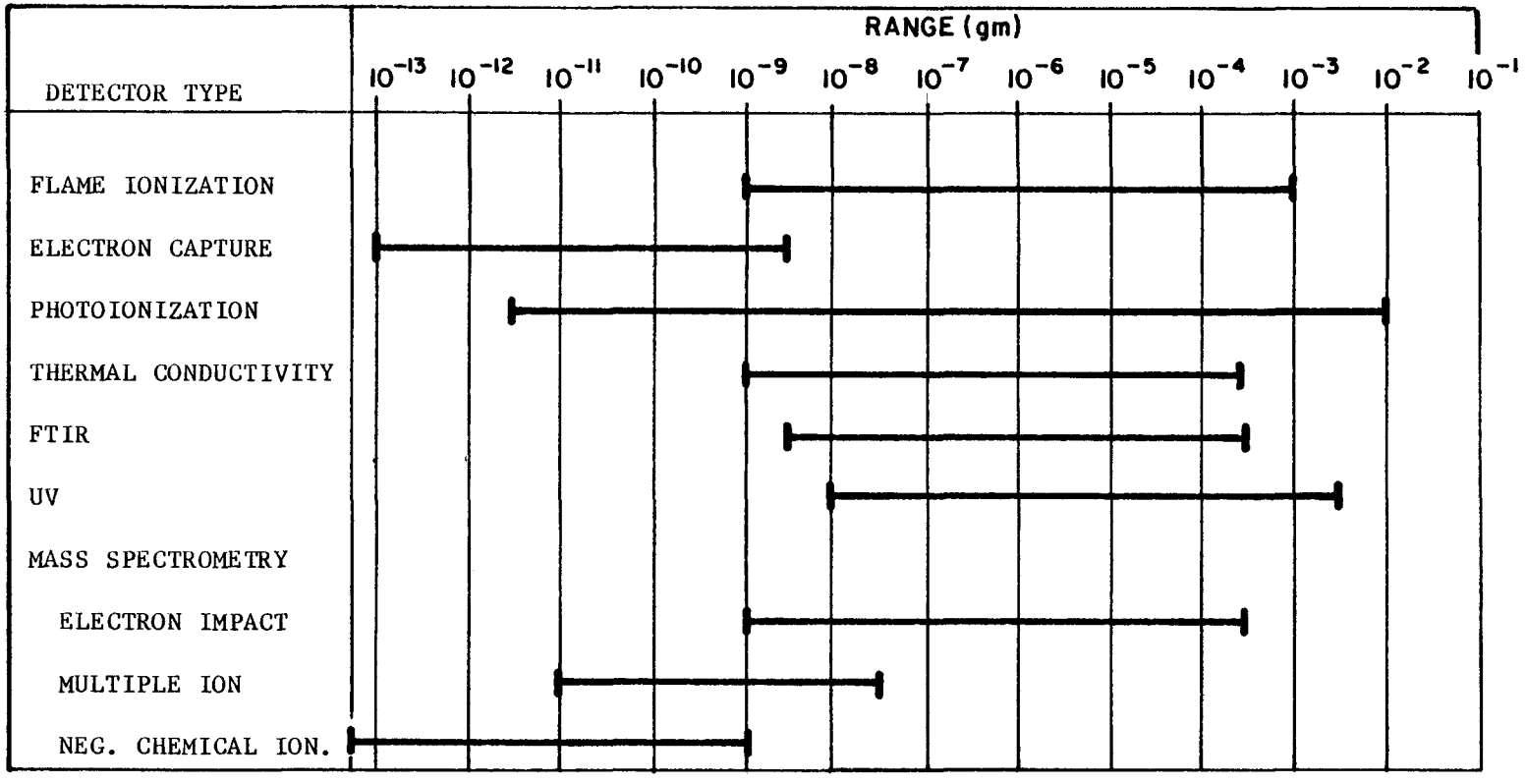

Figure 11. Dynamic Range for Organic Species Instrumentation.

GC and a MS spectrometer, is not yet available. It is expected that if continuous sample concentration techniques are more frequently used, reliable resins and sample extraction systems will be developed. Also likely is the development of more sensitive continuous monitors.

Adaptability is also very dependent on sample conditioning requirements. With present sensitivities, dilution methods of sample conditioning are not appropriate. Particulate removal is required for all organic analyzers. Mechanisms for particulate removal are well developed, however the effect of particulate removal on the integrity of the organic sample is not well documented. HCl gas concentrations of up to 17 percent must be reduced below 1,000 ppm for most presently available instrumentation to ensure a reasonable instrument lifetime. Instruments that can withstand high acid gas concentration are available and instruments presently sensitive to HCl can be adapted for higher concentrations by specifying different materials of construction of key components. Moisture removal mechanisms are also well developed and moisture does not pose an insurmountable problem for most analyzers. The loss of soluble organic species in the removal of moisture is of concern. Sample conditioning methods that maintain sample gas temperatures above the boiling point of water and above the boiling points of all compounds of interest are preferred to condensation or permeation drying mechanisms. It is anticipated that a conditioning system consisting only of several particulate filters and heated lines would be required for organic analyzers equipped to handle significant HCl gas concentration.

Gas Chromatography

The most widely used organic species monitor is the GC/FID combination. Advantages of this combination include:

(a) linear response over 6 decades

(b) insensitive to air, H_2O, or inorganic gases

(c) sensitive to all organic compounds

(d) relatively simple and inexpensive instruments are available.

Gas chromatographs are highly adaptable since many variables can be involved in the selection and operation of an instrument. Column lengths, column packing materials, operating temperatures and flow rates and sample handling equipment can all be manipulated to provide the desired results. Instruments are avilable with multiple columns, multiple detectors and multiple sample handling capabilities such that several classes of compounds can be detected rapidly and simultaneously.

Disadvantages of the GC/FID combination include:

(a) high degree of particulate removal required

(b) not real time analysis

(c) requires pure hydrogen, air and inert carrier gases

(d) detector susceptible to corrosion by HCl.

Particulate matter must be removed to lower and lower levels as the sensitivity of the FID is pushed higher. Particulate causes a noisy baseline that could overshadow a response to an organic compound. Some laboratory GC/FID instruments require 1 hour to complete an analyses of one complete sample. Recent advances in high speed microparticulate packed columns has provided response times of 30 seconds where several minutes would normally be required.[16] A continuous monitoring GC/FID could be tailored to provide response times on the order of 1 minute, however separation efficiency and sensitivity may decrease as the response time is decreased. Response times of less than 3 minutes would allow separation and identification of most hazardous compounds expected to be present, however, two or more columns would probably be required.

An FID that is resistant to attack by HCl could be built through use of hastelloy C or Inconel detector plates. Presently, no "off the shelf" detectors, constructed of these or other acid resistant materials (besides stainless steel which is not considered resistant to high concentrations of HCl) were found, however several manufacturers indicated a willingness to construct special detector plates.

A gas chromatograph equipped with an electron capture detector (ECD) has been successfully used in ambient air monitoring applications where sensitivities of low part per trillion for chlorofluorocarbons have been demonstrated over the long term (1975-1981).[17] The Ni-63 ECD is preferred over the tritium ECD for long-term stability and greater precision. This highly sensitive detector is suitable for trace level determination of a variety of hazardous organic species such as PNAs, PAHs, and PCBs. In combination with an FID, a dual range instrument that is sensitive to 12 decades of concentration of organics would result. This dual detector instrument would be ideally suited to continuous monitoring applications where large swings in concentration of organics are expected. The sensitivity of the ECD requires longer restabilization times between large upsets, whereas the FID recovers more quickly. Operating the incinerator within the range of the ECD would document 99.99 percent DRE in most cases, assuming low parts per billion emission rates. For long-term use with high acid gas concentrations, both detectors should be constructed to minimize corrosion problems.

A gas chromatograph with photoionization detector (PID) is presently the most resistant to corrosion of the chromatographic methods. The PID is a nondestructive detector that can be purchased with teflon-coated internals with no decrease in sensitivity. Advantages of the PID include 10 times greater sensitivity than the FID to certain compounds, a linear range of 10^7 (10X greater than FID) and its nondestructive nature. Disadvantages include lower selectivity (inorganic compounds are also detected), drastic reductions in sensitivity due to coatings on the lamp windows and the need for interchanging several lamps of various energies for identification of compounds. A PID in series with an FID is a recently available laboratory

instrument with potential for continuous monitoring applications. The ratio of the PID to FID response is a tool for further identification of a compound not available with the individual detectors.

Radiation Techniques

All organic compounds and most inorganic compounds absorb radiation. Using UV, VIS, or IR analyzers to continuously detect and identify compounds in a complex effluent stream has, to date, been limited. Only certain compounds are monitored, their characteristic wavelengths are scanned, and absorption at these wavelengths is measured. Since no sample separation steps are involved, interfering species may cause erroneous results. Overlapping spectral bands makes identification of compounds difficult in a continuous monitoring situation. Spectral shifts occur from variations of pH and other factors. The adaptability of these instruments to the variable characteristics of incinerator effluents is limited to detection of one or two compounds per instrument. These techniques are widely accepted as useful in the determination of many inorganic gases. Lack of specificity for organic compounds makes these type of instruments less suitable for organic species monitoring.

Other Techniques

Combining instruments is an ideal way to overcome disadvantages. Specificity problems associated with radiation instrumentation are overcome in GC/IR and GC/FTS-IR combinations. GC/MS is widely recognized as a very powerful tool for compound identification. Combination instruments are gaining wider acceptance as continuous monitoring tools, however, at present the high cost of such systems has limited their use to mostly research application. These instrument combinations are not considered as presently available continuous monitors, however as the technology develops these instruments may be available as monitors in the near future.

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16. ABSTRACT The report gives results of an adaptability study of commercially available sample conditioning and measurement systems, in the form of a guidelines document to be used by EPA and industry personnel. As part of EPA-sponsored research programs to investigate sampling and analysis methods for hazardous waste incineration (focused on adapting existing methods for identifying and quantifying constituents listed in 40 CFR 261), the adaptability of existing continuous emission monitoring systems (CEMS) involves such measurement categories as SO2, SO3, NOx, CO, CO2, O2, HCl, and organic materials. Study results indicate that commercially available extractive continuous monitors can be adapted to incinerators through proper sample conditioning. Available CEMS provide the ranges and sensitivities needed to accurately measure concentrations of the organic and inorganic components of interest.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Samples	Pollution Control	13B
Monitors	Treatment	Stationary Sources	14G
Incinerators		Continuous Monitors	
Wastes		Hazardous Waste	
Toxicity		Sample Conditioning	06T
Measurement			14B

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