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AIR-POLLUTION-MONITORING INSTRUMENTATION

A SURVEY



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AIR-POLLUTION-MONITORING INSTRUMENTATION

A SURVEY

By Alvin Lieberman
and Peter Schipma

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FOREWORD

The purpose of this survey is to aid in transferring air-pollution-monitoring technology developed in aerospace research to the general industrial domain. The authors garnered information from two sources. First, a comprehensive literature search was made, resulting in the bibliography included. Second, NASA centers and industrial and research organizations were contacted. Thirty-two instruments and techniques, originally developed for aerospace needs, were covered in this survey. These were items found to be novel and/or improvements in the area of air pollution monitoring. A summary of the state of the art in this field precedes the discussion of the above items so that the aerospace-developed items can be compared to current practice.

The Technology Utilization officers at the NASA centers organized information and arranged for the authors to meet with the innovators. These officers at the centers may be contacted for additional information if necessary.

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Current State of the Art

The three general problem areas in air pollution monitoring that must be considered to determine the transferability of aerospace techniques to generalized air pollution technology are: (1) the definition of air pollutants in the ambient air, (2) the definition of air pollutants being emitted from a source, and (3) the definition of the atmospheric conditions that govern the rate of transfer from the source to the ambient air. The pollution levels to be examined in the ambient air are several orders of magnitude lower than those emitted from a source such as a stack. Sensitivity and specificity requirements, which are not imposed on source monitors, are thus imposed on ambient-air-monitoring systems. On the other hand, the environmental conditions for a source-monitoring device are often much more severe than those for ambient-air monitors. In general, both ambient-air- and source-monitoring systems must analyze for composition of the sample and/or quantities of particular materials. Monitoring systems for meteorological conditions observe the physical conditions of the atmosphere through which the pollutants are transported. The three air-pollution-monitoring instrument classes are different but are inter-related insofar as their applications and limitations are concerned.

To illustrate some of the differences, a typical ambient-air-monitoring station and its requirements may be compared to a stack-monitoring installation and its requirements. The ambient-air-monitoring station may include requirements for: (1) determining the mass concentration of total airborne particulate materials without regard to their composition; (2) collecting and analyzing specific airborne particles, such as fly ash from coal, fly ash from oil, specific metal oxide fumes, sulfuric acid (H_2SO_4) droplets, radioactive materials, bacteria, or carcinogenic organic compounds in solid or liquid form; and (3) monitoring the mass of dust particles that have settled on a unit surface area of retentive liquid or adhesive surface (subsequently, the settled dust will be monitored for classes of materials, such as water-soluble or organic-soluble materials).

A gas-analyzer system for such an ambient-air-monitoring station may include the requirement that specific gases be sampled and collected for subsequent analysis or that they be analyzed in situ. The

gases of concern may include sulfur oxides, nitrogen oxides, carbon monoxide (CO), halogen compounds, and organic vapors and permanent gases. In the case of solid and liquid particles, concentrations are of the order of several hundred micrograms per cubic meter ($\mu\text{g}/\text{cu m}$), while the gases to be analyzed are in concentrations from fractional parts per billion (ppb) up to 100 parts per million (ppm). At the same time, meteorological conditions measured at the ambient-air-monitoring station may include temperature, relative humidity, wind velocity, and barometric pressure. In some cases, a balloon-borne or mast-mounted, vertical-profile measurement system may be included.

A stack-monitoring system is usually mounted on a stack platform as much as several hundred feet above the ground. The environmental conditions within the stack may be extreme; for example, when the sample inlet is at a temperature of several hundred degrees Fahrenheit, the exterior system for sample transport, retention, acquisition, and so forth may be at a temperature of 40° F. Acid fumes, rain, snow, and other severe environments require that stack-monitoring and analytical instruments be well protected, sturdy, and capable of withstanding extreme conditions.

The major requirements to date for determining particulate emissions from a stack or other point sources have been for the gravimetric analysis of particles whose chemical characteristics are generally known. In some cases, optical density of a collected sample or of particles emitted across a stack plume may be measured. Analytical instrumentation for emitted particles is seldom needed. Concentrations up to several grains of dust per cubic foot are often encountered in stack emissions.

Gases emitted from stacks are analyzed with an in-place stack monitor by collecting them on suitable adsorbents, or in a freezeout trap, or by bubbling them through a suitable absorbing fluid. The gases analyzed include carbon dioxide (CO_2), sulfur oxides, nitrogen oxides, organic vapors, halogen compounds, and so forth. In recent years the use of optical systems permits in situ or remote analysis of infrared absorption for particular gases, which makes the analysis of gas composition from an emitting source practical and allows the determination of gas concentrations under optimum conditions.

The preceding comments indicate the breadth of the requirements for air pollution instrumentation in terms of problems and environmental conditions. However, these comments imply that the sample to be analyzed is already in the analytical system. The peripheral problems of sample acquisition, transport, and treatment must also be considered.

The first requirement of an analysis is that a sample be representative. This means it should represent all of the pollutants in the environment being sampled and illustrate the relationship between the pollution and the environment (concentration and distribution). This relationship may be a matter of temporal or spatial concentration in an environment. A sample size must be selected that is dependent on the sensitivity of the analytical technique and the minimum pollutant concentration. The sample size may range from a few cubic centimeters to several thousand cubic meters, depending on the nature of the problem.

The rate of sampling is determined by the nature of the sample-collecting device, the pressure drop across the sample collector, and the available power. The duration and frequency of sampling depend on the information desired for the particular pollutant-control problem. Because, in most cases, pollution damage is a function of dose (concentration $\times$ time), dose limits must be indicated to guide the selection of sample-period durations. The frequency of sampling should be based on the physical phenomena being monitored. Sampling frequency for a continuous process may be much less than for a chemical process that is operated in a cyclic manner. The duration of sampling periods depends on the significant concentrations, the sampling rate for the particular device used, and the limitations of the analytical procedure to be used. If a sample is to be transported through a sampling line, particle losses and interactions in the sampling line caused by turbulent deposition and agglomeration must be minimized by choosing a sample-line dimension that permits an optimum sample velocity (1500 to 3000 ft/min) in the sample duct. In this way, losses caused by gravitational and inertial deposition, turbulent diffusion, and so forth are minimized.

Appending a series of collection devices to a sample line is often necessary if an air-pollution-monitoring station is required to analyze more than one constituent. It may be necessary, for example, to differentiate between gaseous and particulate forms of related compounds. In differentiating between gases of different boiling points, a series of cryogenic fractionating collectors, each maintained at a lower temperature than the preceding collector, may be needed. If particles are to be collected from the sample by filtration before it enters a gas-absorption system, the filter material must be nonreactive with any of the gaseous components.

Once the parameters of sampling, collection, and/or analysis have been established, the inherent limitations in the analytical or the instrumental procedure must be considered, as they apply to collection efficiency. Particle collection efficiency must be maintained at a minimum of 85 percent for any analytical device. Typical limitations are

that particle sampling devices remove large particles more efficiently than small particles and that the collection efficiency varies with flow rate for many gas- and particle-sampling devices. These considerations do not apply to in situ observation with an optical device that does not require collection of the sampled material. Analogous errors, however, may occur in terms of the optical- or electronic-system instability and presence of interfering materials.

Once the pollution sample has been collected, reliable microanalytical procedures are available for detecting and measuring almost all air pollutants. However, it is necessary to remove interfering substances by pretreatment or to eliminate their effects. Also, it must be realized that the materials being analyzed are not necessarily those discharged from a source. Reactions and alterations in the atmosphere, as well as in storage after sampling, may change the sample after it has been collected. Such alterations may include evaporation of small droplets, dissolution of materials in moisture absorbed from the atmosphere, and reaction of materials that have been collected concurrently. For this reason, the time interval between collection and analysis must be kept as short as possible, or, at least, of constant duration when a series of samples is to be analyzed. The samples should be protected from exposure to heat and light and should be retained in inert containers.

No more than reasonable measurement accuracy should be specified. One should consider not only the inherent limitations of a sampling or analytical system in specifying the required accuracy and precision, but also the change in concentration before noticeable effects occur. Enforcement monitoring systems have more stringent requirements than those of operating monitoring devices, and these should also be considered in specifying accuracy and precision limits.

A final series of general problems in analytical sampling devices includes those of optimum reliability, minimum cost, minimization of required personnel skills, ease of access, and length of service life without requiring excessive reagent, chart paper, filter tape, or other component replacement.

The range of problems, such as the background against which any air pollution instrumentation must be considered, is quite broad. One must also consider system characteristics such as the type of monitoring required, the environment to be monitored, the data to be produced, the use to which data are to be put, and the device limitations that might be expected.

GAS AND VAPOR ANALYSES

Gases and vapors probably represent the largest fraction of total pollutants in the atmosphere. Hydrocarbons from automobiles and

sulfur oxides from thermal power generation are responsible for much atmospheric pollution. Local concentrations of materials that are hazardous to health probably represent the most serious monitoring problem because the levels at which health hazards occur are not known for specific pollutants. The analytical methods must be capable of providing meaningful data for gas concentrations that may be in the parts-per-billion range and for a variety of materials.

Wet-Chemical Analysis

Some of the most common pollutants are analyzed by wet-chemical analysis. Sulfur dioxide (SO_2) is usually analyzed by a colorimetric method known as the West-Gaeke method. A color change is observed with a photometer. Concentrations to 0.01 ppm can be analyzed, but interferences sometimes occur from nitrogen oxides. A minimum gas sample of 2.5 liters is usually required, and an analytical time allowing hourly sampling intervals can be obtained. An analog readout is delivered from the photometer. An automatic colorimetric device that requires only periodic addition of reagents can be purchased for approximately \$5000 (ref. 1).

SO_2 in ambient air can be titrimetrically determined in a concentration range from about 0.01 to 10 ppm by oxidizing the SO_2 in hydrogen peroxide (H_2O_2) to sulfuric acid (H_2SO_4) and titrating. A sample size of approximately 1 cubic foot of air is required. Analytical time is approximately 10 minutes, and manual operation is involved (ref. 2).

Automated conductometric analysis is often used for SO_2 measurements from the atmosphere. In this method SO_2 is collected in an acid solution and oxidized to H_2SO_4 by H_2O_2 . The method is sensitive in the range of 0.01 to 2 ppm. Materials that form strong electrolytes in solution interfere. The sample size is approximately 10 cubic feet of air and the analytical time is approximately 10 minutes. The data readout is analog, and the cost of a commercially available instrument is approximately \$5000 (ref. 3). There are many additional methods of measuring SO_2 , but the above are the major analytical methods for this gas.

Hydrogen sulfide (H_2S) can also be analyzed by a wet-chemical colorimetric method. Methylene blue is produced by a reaction with suitable reagents, and concentration of H_2S is determined by measurements of optical absorption (ref. 4). Sensitivities in the parts-per-billion range have been reported. Sample sizes of some 30 cubic feet are required with an analytical time of approximately 2 hours. Data are obtained by photometric readout; although analog data are obtained, this system has not been successfully adapted for automatic instrumentation.

The existence of nitrogen oxides is determined by dye formation using the nitrite ion (NO_2^-) as part of the reaction (ref. 5). The sensitivity of this method ranges from a few parts per billion to about 5 ppm. Sample sizes up to $\frac{1}{2}$ cubic foot produce sufficient color change for meaningful results. The analytical time is approximately 1 hour. Photometric readout is obtained, but no automated instruments have yet been developed for this procedure.

Oxidizing gases, such as ozone, are analyzed by observing color change after absorption in potassium iodide (KI) (ref. 6). The oxidants can be analyzed in the range of a few parts per hundred million to about 10 ppm. A sample size of approximately 2 cubic feet of air is suitable, and analytical time of up to 1 hour is required. The photometric readout produces analog data, but the overall procedure is manual.

Hydrogen fluoride (HF) and other volatile fluorides are analyzed colorimetrically after titration or spectrophotometrically (ref. 7). Concentrations below $1/100 \mu\text{g}/\text{cu ft}$ can be analyzed. An air-sample size of approximately 10 cubic feet is the minimum and, in some cases, 100 cubic feet is required. Analytical time is approximately 7 hours because a detailed procedure is required to eliminate interferences that are caused by a large variety of materials. These are removed by double distillation with perchloric acid (HClO_4). Analog data are produced by the photometer or colorimeter, but the method is manual.

A number of materials including SO_2 , nitrogen oxides, oxidants, chlorine (Cl_2) or chlorides, and fluorides or cyanides may be measured by modified wet-chemical procedures in a system of gas absorption followed by colorimetric analysis. Continuous analyzers using programmed sampling valves, proportioning pumps for reagent delivery, heating baths, distillation columns, temperature control, colorimeters, and so forth, can be purchased (ref. 8). Sensitivities and sample sizes for these colorimetric instruments are equivalent to those given for the manual methods, and analytical time is of the same order as that for the manual methods. Reliability, of course, is much less, and analog data are produced for the colorimetric readout. The cost for a complete system capable of analyzing a number of gases may run as high as \$70 000 to \$80 000.

Most organic gases are analyzed by instrumental methods. Volatile organic substances containing oxygen are usually analyzed by colorimetric methods. Analyses are reported, for example, as "total aldehydes," in which a number of individual aldehydes and ketones may be present (ref. 9). Sensitivities of several parts per million are reported with sample sizes of a few cubic feet. Analytical time is of the order of 1 hour with analog readout using colorimetric analysis.

Spectrographic Analytical Method

Spectrographic and spectroscopic analytical methods are used primarily for particulate materials that have been collected and can be placed in a spectrograph or an emission spectrometer. A number of gases and vapors, however, can be analyzed by such methods as emission and fluorescence spectroscopy. An example of one of these methods is the use of detector elements for chromatographic columns; these elements utilize flame emission to characterize the materials passing through the column.

Organic vapors can be detected by a flame-ionization analyzer (ref. 10). The flame-ionization analyzer responds in proportion to the number of carbon atoms in a gas sample. Sensitivity below 1 ppm can be obtained depending on the gas being analyzed. Sample sizes down in the cubic-centimeter range can be used, and analytical time is essentially zero with real-time data production. The type of data produced is analog. Depending on the gas concentration and type of analyzer, costs in the thousands-of-dollars range can be expected.

Both organic and inorganic vapors have been analyzed by mass spectroscopy (ref. 11). Monopole, quadrupole, and time-of-flight instruments have been used for gas analysis. Concentrations to several parts per million can be analyzed. Sample sizes of a few hundred cubic centimeters are adequate, and analytical time is of the order of 5 to 20 minutes, depending on the complexity of the analysis desired. An instrument can be set to scan for mass numbers from one to several thousand. The scan rate is usually of the order of 20 minutes to 1 hour, and printout is digital. The cost of such an instrument can be several tens of thousands of dollars.

The infrared absorption characteristics of several gases and vapors make it possible to detect and analyze their presence in the atmosphere with continuous analyzer systems. CO can be analyzed with a sensitivity of approximately 1 ppm in a nondispersive infrared analyzer (ref. 12). A sample size of approximately one-half cubic foot can be used, and analytical time is of the order of seconds. Data produced are analog, and the cost for a typical analyzer is several thousand dollars. Similar instruments of the same design have been used for analysis of organic materials. Dispersive infrared spectrometers have also been used to determine hydrocarbon emissions based on absorption at the 3.4-micro wavelength (ref. 13). Interferences occur that can be avoided in the nondispersive infrared-sensitized systems, but other characteristics of this analytical procedure are the same as for a non-dispersive infrared analyzer.

A third type of infrared analysis has been recently described in which correlation spectroscopy is used (ref. 14). In this system, a spe-

cific compound is analyzed by comparing the infrared spectrum of an unknown gas to the infrared spectrum of a known material. Sensitivities of approximately 20 ppm are claimed. The device has the advantage of being suitable for use as a remote sensor using the Sun or other radiant-energy source to pass energy through a particular pollutant plume. Recently a passive infrared-analysis system has been studied in which a heated stack plume emitted enough infrared energy over the background so that it served as its own infrared energy source.

Ultraviolet absorption can be used to detect unsaturated hydrocarbons. A recent development of a Geiger counter for detection of low energy photons has permitted development of a field analyzer that is capable of detecting hydrocarbons in the atmosphere. The sensitivity of this device is 2 ppm. Sample flow rates of several hundred cubic centimeters per minute are used, and real-time analysis is possible. Analog data are produced, and the cost of the device is in the \$1000 range.

Thermal Conductivity Measurement

The concentrations of several gases can be determined by measuring the thermal conductivity of the sample gas as compared to that of a known reference gas. Four filaments, arranged as an electrical resistance bridge, are heated, and imbalance caused by changing gas compositions is reported as a temperature difference. Sensitivity to approximately 0.1 percent can be obtained with a gas-flow rate of approximately $\frac{1}{4}$ cu ft/min. Analytical time in the minutes range is normal for data in terms of relative concentrations based on a calibrating or standard gas. Cost for such an instrument is approximately \$500.

Chromatographic Analysis

Chromatographic analysis is probably the most generally used method of measuring and detecting gases in the atmosphere. It is capable of separating, in suitable columns, essentially all of the polluting gases, both organic and inorganic, that may be present in the atmosphere. In brief, the method utilizes a column through which a mixture of gases is passed. The difference in the mobility or the diffusion rate of the component gases in the mixture passing through the column is a function of the molecular structure of each gas. Selection of a suitable detector from the six or more available detecting devices is based on the composition of the gases to be analyzed. Detectors measuring changes in thermal conductivity have been used along with detection devices involving flame-ionization and electron-capture methods.

In recent years a vast amount of work has been done on gas chromatography for air pollution analysis. A meaningful discussion of all the results of this work is beyond the scope of this survey. To summarize briefly, however, sensitivities in the parts-per-billion range can be obtained, and sample sizes from a few cubic centimeters to several cubic meters of gas are usable. Fractionating freezeout methods along with representative absorption sampling can be used to obtain gas samples for injection into the chromatographic column. The analytical time is normally of the order of 20 minutes. The data obtained are digital. The cost of a usable gas chromatographic system ranges from several thousand to several tens of thousands of dollars, depending on the number of columns, degree of automation, and the readout devices used.

GAS AND VAPOR CONTROL METHODS

There are four principal methods of controlling the emissions of vapors to the atmosphere. These are absorption, adsorption, incineration, and catalytic combustion.

Absorption

Absorption is a basic chemical engineering unit operation, which is frequently referred to in the air-pollution-control field as "scrubbing." It is a diffusional process involving the transfer of gas molecules to a liquid phase. Concentration differentials at the interfaces serve as driving forces, and the process is favored by high-interfacial surface areas, turbulence, and high diffusional coefficients. Because some soluble component of a gas mixture is to be dissolved in a liquid, the absorbent chosen should have high solubility for, or react irreversibly with, the absorbed gas.

Equipment used for the absorption of gases can be placed in five categories. These are packed tower, plate tower, spray chamber, venturi scrubber, and jet scrubber.

In a packed tower, crushed rock, Raschig rings, burl saddles, and various other materials and shapes are used for packing. The liquid is usually introduced at the top of the packing and trickles through the layers of packing that provide the necessary large surface area. The contaminated gas flows upward through the packing, contacts the absorbing liquid, and leaves cleansed at the top of the packed tower. The liquid commonly used is water, but solutions of neutralizing chemicals, organic solvents, oils, and emulsifiers are also employed.

A plate tower is usually cylindrical with several sections of perforated horizontal plates; the two most common are termed "bubble caps" and "sieves." In a plate tower the gas-liquid contact takes place in a

series of steps (at the plates) rather than continuously as in a packed tower.

The simplest spray chamber consists of a cylinder in which spray nozzles are mounted in the upper section and droplets are forced downward by a liquid flowing down the interior walls of the chamber. Although the liquid and gas flows may be cocurrent, the gas stream is usually introduced tangentially at the lower section of the tower, so that a spiral motion is imparted to it, and the liquid sprays are directed radially. In this way, the spray is directed centrifugally to the wall from which it drains as a film flow. Simple spray towers can be either countercurrent or cocurrent in operation, have a relatively low pressure drop, and are not subject to plugging, as are packed columns and plate towers. Some spray towers have been successful in the absorption of relatively insoluble gases; but because the mixing of spray and gas is not as vigorous in the countercurrent towers as in other equipment, such as a venturi scrubber, spray towers are perhaps best suited to applications involving easily absorbed gases.

The venturi scrubber is essentially a spray tower in which an effort is made to maximize the mixing of the gas stream passing through the main section of the venturi by introducing a liquid at the throat of the venturi. In the venturi scrubber the gas stream passes at a high velocity through the venturi, with the scrubbing liquid being introduced at relatively low pressure at the venturi throat where the liquid is sheared and droplets are formed. Contacting is essentially cocurrent with the flow energies being separately supplied for the gas and for the liquid. The energy required for forming droplets and for intimate mixing with the gas is furnished by the gas stream. The liquid is introduced at conventional line pressures. The resultant liquid spray mixes with the gas, a degree of absorption takes place, and an entrainment separator—usually of the simple centrifugal or spray type—must be provided at the venturi discharge to remove liquid from the washed gases. The pressure drop across the venturi scrubber ranges from 10 to 100 inches of water with gas velocities at the throat exceeding 5000 ft/min. The high pressure drop in the gas stream results in a high power cost, and necessitates high tip speed on the main fan with an increase in problems of erosion, noise, or rotor imbalance.

The liquid jet scrubber is essentially an ejector designed as a fume scrubber. Energy is imparted to the liquid spray, which, through an aspiration effect, produces the suction necessary to move a waste gas and also succeeds through intermixing or surface-area contact in removing an amount of absorbable gases. The capacity of such scrubbing equipment can be varied by changing the liquid flow rate or designed characteristics at the venturi. A droplet entrainment is required at the discharge end. In such scrubbers, water at about 100 lb/in.

generates pressure differentials of the order of a few inches of water, and gas-flow rates do not usually exceed 1000 cubic feet min/unit scrubber.

Generally, the two-film absorption theory is used for the design of absorbers and interpretation of performance. In this design approach, the assumptions are that (1) the transfer rate is proportional to concentration differentials at the interfaces, (2) equilibrium conditions exist between the gas and liquid at the interface, and (3) no holdup or interfacial resistance to flow exists.

In general, packed towers are prepared for small installations, for use with corrosive gases, high-forming liquids and high liquid/gas ratios, and for low-pressure-drop requirements. Plate columns are frequently more economical than packed towers because their ability to tolerate higher gas velocities allows use of smaller diameter columns. They can handle liquor rates that would flood typical packing, are less susceptible to plugging, and can be equipped to cool the liquor to remove heat of dilution, either with cooling coils on the plates or with external coolers. Spray towers are of particular importance when the pressure drop is a major consideration and when dust particles are present in the waste-gas stream.

Adsorption

In atmospheric pollution control, the principle of adsorption is employed primarily to prevent highly odorous or offensive organic vapors from escaping into populated areas. Adsorption systems are widely used in industry to remove gases and vapors that can produce human irritants, obnoxious odors, fire hazards, explosive reactions, unhealthy conditions, hazardous concentrations, unsafe operations, undesirable products, corrosive atmospheres, and inadequate processing. Solvent recovery, odor control, removal of gaseous contaminants, protection against gas-warfare and hazardous chemical reactions are suggested candidates for adsorption systems. Food services, hospitals, laboratories, petrochemical manufacturers, chemical users, printing plants, fallout shelters, and atomic energy installations are some of the users of adsorption systems to prevent air pollution or to eliminate pollution of the premises and processes by intake air. Because adsorbents are versatile enough to solve these problems, the list of possible air pollution applications is extremely long.

In air pollution control, the principal use of adsorption is for the physical adsorption of gaseous matter on solids in dynamic systems. Physical adsorption is defined as the capture and retention of molecules from the gas phase by the surfaces and capillaries of solid adsorbents. Physical adsorption is completely and easily reversible; the

adsorbed material is removed by high temperature and/or low pressures. Thus, adsorption systems are capable of being regenerated.

Although a great variety of clays, chars, gels, oxides, silicates, and activated carbons have been used as sorbates, activated carbons have been the subject of the most effort and application in air pollution abatement. Because physical adsorption has basically been a surface phenomenon, the more surface area per unit volume that is obtained, the more effective the adsorbent. Adsorbents display a specificity, or differential affinity, for various materials. Fortunately, many of the specificity relationships have been established by experience in the field. For example, activated carbons specifically adsorb hydrocarbon vapors in preference to water vapor, while silica gel specifically adsorbs water in preference to hydrocarbons.

One-pass nonregenerative dynamic systems are used when average contaminant concentrations are of the order of a few parts per million or less. Although the systems are designed to take contaminant slugs up to 1000 ppm, it is not economical to use this type of adsorber on concentrated contaminant gases. Holding capacity in one-pass dynamic adsorber systems is generally 5 to 20 percent of adsorbent weight; that is, in the case of an easily adsorbed vapor, the contaminant breakthrough does not occur until total vapor pickup exceeds 20 percent of the adsorbent weight. Because one-pass nonregenerative adsorber elements usually contain highly active and relatively expensive adsorbents, the replacement cost or factory reactivation becomes burdensome if the system is used to remove high concentrations of contaminants.

One-pass regenerative adsorber systems are used when the concentration of contaminant exceeds a few parts per million. Two adsorber vessels are usually employed with one adsorbing while the other is being regenerated. In reactivation, low-pressure steam is normally used to raise the temperature of the adsorbent bed and drive off the adsorbate. Steam and adsorbate are usually condensed together for recovery or disposal. Steam also acts as a stripping vapor; because a portion of it condenses in the adsorbent, the bed temperature is reduced by evaporation of the steam during the adsorption cycle. Bed-temperature increases created by heat of adsorption must be dissipated when handling heavy concentrations of contaminants; otherwise the efficiency and/or holding capacity of the bed is seriously reduced.

The original equipment cost for adsorption systems, excluding the erection cost, is approximately \$32.50 per pound of contaminant. Operating costs on a nonregenerative system include replacement or factory reactivation of the adsorbent, maintenance of the bed holders and frames, air movement, space occupied, transportation to and from the factory, and labor to remove and replace elements. Replacement or

factory reactivation and factory maintenance charges on bed holders are estimated to be of the order of \$10 per pound of contaminant retained. Assuming a typical bed pressure drop of 1.5 inches of water, 0.75 brake horsepower (hp) is required for every 1000 cu ft/min of capacity installed. For a regenerative system, additional equipment is required to generate steam, such as a cooling-water system, dry-air heaters, and additional fans or air pumps. Rough estimates of equipment capacities for the costs above are:

Equipment	Capacity
Steam generating.....	3 to 5 lb/lb of vapor retained
Cooling water system.....	7 to 10 gal/lb of vapor retained
Dry heat.....	0.10 to 0.15 kw hr/lb of vapor retained
Air moving.....	5.0 brake hp/1000 cu ft/min of air

Incineration of Gases and Vapors

Incineration is rapid, high-temperature oxidation in the gas phase. Contaminated gases and liquid wastes are incinerated for odor control, reduction in opacity of plumes, reduction in emission of reactive hydrocarbons, and reduction of explosion hazards.

Many of the waste materials disposed of by flame afterburners are liquid aerosols, and the fuel for the afterburner can be a liquid such as oil. In the afterburner the actual combustion occurs between oxygen and the vapors, or gaseous decomposition products, of the waste and fuel liquids. In the combustion of hydrocarbons, a complex series of chain reactions plays a predominant role. At the high temperature of flames, hydrocarbons disassociate into radicals that in turn recombine. There is evidence that the radicals—OH, HO₂, H, and O—produced in the oxidation of hydrogen are important chain carriers. Thus, aldehydes and other oxygenated organic compounds are present in the stepwise oxidation of hydrocarbons, and these intermediates will appear in the end products if anything disrupts the chain reactions and prevents their ultimate combustion to form CO₂ and H₂O. These oxygenated materials tend to be irritating and odorous and are unwelcome products in the effluent.

Important factors in the combustion process are reaction time; temperature, which increases reaction rate; and turbulence, which provides thorough mixing of oxygen, intermediate products, and chain carriers.

Flame combustion, as a method of air pollution control, has been applied to a variety of processes and effluents including flares and furnaces for disposal of waste gases and liquids from coffee roasters, smokehouses, rubber curing, cupola gases, rendering plants, varnish

kettles, enamel baking ovens, asphalt blowing, and printing-press vents.

The yearly capital and operating costs for a flame incinerator on a continuous roaster is about \$22 000. Approximately three-fourths of the cost is for fuel for the disposal of halogenated hydrocarbons. A flame incinerator capable of handling 4 to 7 gal/min of waste is reported to cost \$250 000, with operating costs about 6 cents per gallon of waste. This cost is compared to 10 cents per gallon for disposal by drum burial.

Catalytic Combustion

Direct-flame incineration, as a method for the disposal of organic vapors and gases, is often limited in application because of the excessive cost of the high temperature required. The high-ignition-temperature requirement can be overcome by passing the waste gas stream through a catalyst bed, because the catalyst causes the reaction to occur below the normal combustion temperature and does not become part of the end product. The process lessens the temperature necessary for the exothermic reaction of organic vapors or gases with oxygen by as much as 500° F. The chemical union of oxygen with the organic fumes occurs without flame on the surface of the catalyst. The temperature rise of the waste gas stream after passage through the catalyst bed depends on the Btu value of the fume.

Many substances have catalytic properties and are used for this purpose. Metals of the platinum family are generally chosen for effluent control because they produce the lowest catalytic ignition temperature. Sufficient surface area must be available to permit completion of the oxidation reaction within the catalyst bed. Normally, catalyst surface areas of 0.2 sq ft/cu ft/min are utilized, although certain difficult applications may require as much as 0.5 sq ft/cu ft/min.

The catalytic combustion method of fume disposal has a wide range of industrial applications in such diversified manufacturing activities as foundry-core baking; fish-oil and animal-fat rendering; solvent evaporating; oil refining; paper printing; and varnish, chemical, and plastics manufacturing. The method can be usefully applied to paint-baking ovens, if the paint does not contain volatile catalytic poisons. Satisfactory results have been obtained in the combustion of low-boiling hydrocarbons; of heavy vapors liberated in the cooking of oils, tars, and asphalt; and in the chemical reduction of nitrogen oxides under reducing conditions.

The catalytic method has been found to be unsuitable when the exhaust fumes contain such particulate material as fly ash, inorganic solids, or vaporized metals. These materials cause a rapid deterioration of the catalyst with resultant excessive maintenance and replace-

ment costs. For this reason the exhaust gases from foundry cupolas, blast furnaces, and coal-fire boilers cannot be handled by catalytic methods. Some halogenated hydrocarbons and silicone paint additives are also harmful to the catalyst.

Properly designed catalytic combustion units have been operated with very acceptable efficiencies; disposal of various hydrocarbons and other organic vapors has exceeded 98 percent efficiency in some installations. A distinct advantage of this method over furnace combustion is that practically no nitrogen oxides are produced. Catalysts have been used, in fact, to reduce nitrogen oxides to nitrogen in waste-gas streams.

The initial costs of catalytic combustion units, including installation, vary widely with each installation requiring a separate design study. In general, a cost in the range of \$3 to \$5.50/cu ft/min covers most installations, and the catalyst element is about \$1/cu ft/min. The operation cost of this disposal method covers maintaining the catalyst and system and preheating the fume, which is dependent on the nature of the fume. Maintenance costs include a periodic cleaning to insure proper efficiency and the infrequent replacement of the element. Under normal operation a platinum catalyst element should be inspected every 6 months; immediate inspection should be made if abnormal operation is observed. Dust and dirt may be removed from the element by immersion and agitation in hot water containing detergent. Elements coated with oils or resins should be heated to 1100° F, cooled, and treated in a nitric acid (HNO_3) bath. With proper maintenance, the catalyst may last several years with no loss in efficiency.

PARTICLE-COLLECTION AND MONITORING SYSTEMS

The qualitative nature of the hazard from airborne and settled particles has long been known. However, as in many cases involving chronic exposures, quantitative information is not available concerning the tolerable dose before damage to health or property occurs.

Atmospheric particulate materials, which are often generated by industrial processes, may contain or be composed of toxic, corrosive, and erosive compounds. Their presence in the atmosphere or on sensitive surfaces may not only reduce visibility but also cause damage to health, to appearance, and to plant life. In London, a man was executed in 1306 for burning coal while Parliament was in session.

Present monitoring systems are designed either to meet legal limitations or to obtain sufficient information about the nature of the particulate air pollution to permit remedial action. Thus, the present systems are used to observe the particulate debris that is deposited on horizontal or vertical surfaces, to observe the particles suspended in

the ambient atmosphere, or to monitor the vents and stacks associated with a process that may cause emission of particulate debris.

It should be emphasized that scientifically justified limitations on tolerable levels of particulate air pollution are not quantitatively known. The complicating factors such as environmental conditions, contributing pollutants, synergistic effects, collection site status, and health deterioration or damage cannot be specifically stated for any single air pollutant or for a simple combination of air pollutants. Limitations have been set by industrial hygienists concerned with such aspects as control of radioactive hazards. Maximum-acceptable-concentration (MAC) limits have been set for 8-hour exposures of healthy working male individuals in reasonably controlled environments. These limits, however, are not useful for generalized air pollution control.

Air pollution results in exposure of the entire cross section of population from strong, young men to newborn infants under environmental conditions that are widely variable and uncontrolled. The best MAC limits are only one part of the input for finding the tolerable air pollutant levels. Combinations of materials may act in a synergistic manner not completely defined. Even more important, long exposure times at low levels have not been adequately studied.

Esthetic considerations involved in seeing a clear view as compared to a smoky view are also of real, but unmeasurable, importance in setting air-pollutant-concentration limitations.

When a qualitative analysis of particulate contamination is required, a quantity of particles is usually collected and analyzed by procedures similar to those used in any analytical laboratory. Physical measurements range from direct observation of the particles in the atmosphere and of their effects as they deposit or interact with various substrates to indirect observation of interactions between the particles and the means of measurement. The techniques ranging from routine to conceptual are in varied states of development.

Present instrumental techniques are capable of very high sensitivity for analysis of particulate contamination. An excellent sensitivity is required because of the lack of quantitative information for tolerable contamination levels. In general, the analysis of particulate contamination is based on physical measurements.

In categorizing the instruments used for monitoring particulate air pollutants, the methods in terms of instrument types, of monitored pollutants, of effects of monitored pollutants, or of instrumental applications may be considered. The authors have chosen instrumental applications as the most useful way to categorize the instruments used

in the examination of settled particles, of airborne particles, and of the emitting sources considered.

The settled dust particles from the atmosphere may have irritating and corrosive effects and are usually very obviously present. They are usually measured and reported in terms of mass of material of several types per unit area. Sizes of airborne particles permit inhalation and retention in the respiratory system; thus, health hazards occur. Airborne particles also cause reduced visibility in the atmosphere. These particles are measured in terms of mass per unit gas volume, number of particles per unit gas volume, or, indirectly, as a visibility through the atmosphere. Emissions are of interest because they are normally the source of both settled and airborne particles and are a direct indication of the processes that cause air pollution. They are usually measured in terms of mass per unit volume of emission, visibility through the emission, or as mass of materials emitted per specific process or process subdivision.

Instruments used in one monitoring application can often be used in another. However, correlations from one application to another are usually difficult and often impossible. For example, settled dust must come from the atmosphere. In a fixed volume covering a given area, a direct correlation should be found. However, the differences in settling rates for particles of different Stokes' diameters and the presence of random eddy currents through the atmosphere make such a direct correlation impossible.

Some of the instrumental techniques, methods, and devices used to analyze particulate air pollution will be discussed. Particle-collection techniques are applicable to both particle analysis and particle control (collection of particles removes them from the environment). In situ measurement techniques are applicable to analysis only.

Settled-Particle Analysis

Instruments for settled-particle analysis are perhaps the simplest devices. Interpretation of results may be complex because of the diverse nature of the deposition of particulate material in the settled-particle collectors, the so-called "dust jars."

The dust jar is usually a glass, metal, or plastic container, 6 inches in diameter and 8 inches in height. It is placed in a stand at a level where reentrained dust from the normal traffic is not lifted to its interior. A layer of liquid is placed in the bottom of the jar. During winter or inclement weather, antifreeze may be added. A fungicide or algicide should be included to prevent growth of cultures that could change the reported results. Bird guards are usually used to prevent birds from perching on the edge of the jar and adding deposits to the fluid in the jar. Jars are usually left out for a period of 1 month.

Settled particles are analyzed by weight. An aliquot of the liquid is taken after the settled material is thoroughly dispersed. The liquid is evaporated, and the settled material is analyzed in terms of weight per unit area in the jar; the result then is extrapolated to unit weight per square meter or, in some cases, per square mile. It is also possible to extract, with suitable solvents, the organic-soluble and water-soluble components to determine combustible materials, and to report each component separately (ref. 15).

Another device used for determination of settled particulate material is the tacky or adhesive sheet. The adhesive-coated sheet is exposed to the atmosphere for a fixed period of time, ranging from 1 hour to 1 week. The sheet is then examined visually for specific particulate contamination. In some cases, magnification with a low-powered microscope may be necessary (ref. 16).

A variation on the above technique allows the use of nutrient plates for analysis of bacteriological debris, especially in the interiors of hospital rooms. The nutrient plates are exposed for a suitable time period, and viable colonies are visually counted to indicate the level of bacteriological contamination in the atmosphere.

In general, measurement of settled particulate material is helpful in determining trends in air pollution. Trends in airborne particles often follow trends in settled particles and, therefore, long-term changes in air pollution can usually be followed by observing the levels of settled debris. However, quantitative correlations between ambient-air-pollution levels in terms of mass per unit volume in the atmosphere and the total number or mass of settled particles are difficult, if not impossible, to obtain.

Airborne-Particle Analysis

Adequate sampling from the atmosphere is often difficult because the particles suspended in the atmosphere are not uniformly dispersed, do not follow the gas-stream lines in the atmosphere, and are subjected to forces other than purely aerodynamic ones. Before any analytical system is used for monitoring, a suitable representative sample must be obtained from the atmosphere. This sample must: (1) be representative of all particles in the environment, (2) indicate the magnitude of the environment from which the sample has been obtained, (3) be of sufficient size to permit a reasonable analysis, and (4) not be degraded during collection or sample handling.

Adequate sampling of particulate material usually involves isokinetic sampling in which the material to be sampled enters the sampling orifice without being disturbed or accelerated. Normally this means that the sampling orifice aspirates the sample at the same velocity as the sample stream. Anisokinetic sampling produces errors pro-

portional to particle sizes because large particles do not follow changes in the direction and velocity of airflow (ref. 17).

Errors resulting from anisokinetic sampling of suspended dust are tolerable in the open atmosphere but are of extreme concern in sampling from stacks or other emitting sources. Errors resulting from anisokinetic sampling increase with particle diameter squared according to a complex function.

Some of the collecting devices that obtain a sample of particles for a subsequent analysis are considered in airborne-particle-analysis systems.

Filtration.—In the broadest sense, a filter is any coarse structure composed of granular or fibrous materials that will remove suspended matter from a fluid passed through it. When the filtration process is applied in the field of air pollution, the problem always involves fluid flow through a porous medium; the particles deposited on the medium; a resultant decrease in void volume; and a proportional increase in resistance to flow, or pressure drop, as filtration progresses. Some means of periodically removing solids must be provided when the percentage of void volume is rapidly reduced with time. The utility of a filter is governed by how efficiently it collects particulate material without developing excessive resistance to flow.

The filter medium used in any particular application is selected on the basis of the type of analysis to be performed on the collected particles. For example, for visual observation, a surface collection that can be obtained by membrane filter media is desirable. If weight analysis is required, high-flow, high-capacity systems of paper or glass-fiber medium-retaining particles larger than a fraction of a micron are usually used. Fabric filters are one of the oldest and most reliable of the high-efficiency devices available for the collection of dry particulate materials. Their wide acceptance is attributable to a number of advantages, the most important being that they are capable of maintaining 99 percent or better collection efficiency, despite wide variations in properties of the carrier gas. Minor process disturbances or process cycling do not result in a discharge of particulate material to the atmosphere. Fabric filters are simple to operate and maintain, do not require skilled labor, the initial cost is generally lower than that of competitive control equipment with equally high efficiency, and power consumption is moderate.

Major disadvantages of fabric filters are that the temperature is limited to that withstood by the fabric (500° F maximum for fabrics currently available), and that improper application or operation may result in diminishing the flow of gas through the device. The fabric filter must be operated above the dew point of the gas. Major consid-

erations in the selection of a fabric, besides temperature, are resistance to abrasion and resistance to flexing.

Fabric filters operate so that flow through both the fabric and the deposited dust layer is viscous. Thus the fundamental characteristics embodied in Darcy's law apply. As previously stated, the dust collected on a fabric filter must be periodically removed if excessive resistance to flow is to be avoided. The built-up dust cake is usually removed from the fabric by one of three methods: mechanical cleaning using shaking or rapping devices, collapse cleaning accomplished by introducing a slight negative pressure on the interior of the bags, or reverse-jet cleaning in which air jets are used to blow the dust cake from the filter.

The three most important costs associated with fabric filtration are the first equipment cost, power cost, and maintenance cost. Generally, \$2.50 per square foot of cloth area is a good figure for estimating installation cost (exclusive of dust-disposal equipment) for woven fabrics that are intermittently or periodically cleaned. Because this figure is based on cloth area, the cost in a given situation depends on the filtration velocity to be used. Normally, filtration velocities range from $\frac{1}{2}$ to 1 ft/min. Costs for specialized equipment, such as reverse-jet or pulse-air equipment, run higher per square foot of cloth; but because higher filtration velocities are possible, this equipment may be economically advantageous. Cost for the equipment is about \$14 per square foot, but filtration velocities generally range from 3 to 25 ft/min.

For chemical analysis, suitably soluble filter media are selected; but when sampling from high-temperature environments, alundum (porous aluminum oxide, Al_2O_3) and/or glass-fiber filters are used. A wide variety of commercially available filter media is available. After the particles have been collected on the filter media, the technique of analysis can be selected at the discretion of the analyst.

The filter assembly may contain a sequential sampling device in addition to the filter holder, filter media, and vacuum source. These sampling devices, which are commercially available, can be used to obtain information about the time variation in levels of particulate debris in the atmosphere. They are generally paper-tape samplers in which a roll of filter tape is used to collect the debris. The tape is advanced sequentially at preset intervals to permit sampling through a single section of tape for a given time period.¹

¹ Instruments for filter-tape sampling can be obtained from the Gelman Instrument Co., Ann Arbor, Mich.; Instrument Development Co., Riverside, Calif.; Research Appliance Co., Allison Park, Pa.; and VonBrand Filtering Recorders, New York.

The density of a filter-tape deposit can be expressed in terms of light transmission through the deposit. To determine the density of the deposit, the volume of the gas sample is divided by the tape-deposit area, giving the length of a sample-gas column having a specific uniform haze density that would produce the same reduction of light transmission as the deposit. The density is expressed as a coefficient of haze per 1000 feet of air (ref. 18).

Inertial Collection Devices.—An inertial particle collector takes advantage of the tendency of particles moving in an airstream line to continue in the original direction when the airstream line is deflected by an obstacle. The particles impact on the obstacle and can be retained by a suitable adhesive coating for subsequent analysis. Several instruments exist for collecting particulate material by virtue of particle inertia.

A single-stage impactor consists of a substrate for collection and subsequent examination of particulate material. The substrate faces an orifice through which the gas stream that may contain particles for analysis is drawn. This instrument is usually sensitive to particles from approximately 0.5 micron to approximately 50 microns in diameter. High collection efficiency results from the gas particles being accelerated through the orifice; however, the acceleration causes adiabatic expansion. This expansion causes water vapor to condense on the particles being collected, resulting in erratic operation. Instruments of this type range in cost up to approximately \$750.²

The wet impinger is essentially a single-stage impactor. Its efficiency is maintained at a constant rate by continuously washing off the collecting substrate with a stream of liquid. Thus the collected dust particles are moistened and retained in the liquid. The sample is examined under a microscope by wet-chemical or colorimetric analysis or by depositing an aliquot of the sample on nutrient plates for culturing for bacteriological measurements.³

The single-stage impactors require that sufficient energy be imparted to the particles so that the smallest particle of interest is collected. If a large-size distribution is present, the larger particles may be impacted

² Some typical units are the Casella sampler from Union Industrial Equipment Co., Fall River, Mass.; airborne bacteria monitor from Anderson Samplers, Provo, Utah; annular impactor from the Staplex Co., Brooklyn, N.Y.; Konimeter from W. Watson & Sons, Ltd., Barnett, England; and the rotorod collector from Metronics Associates, Inc., Palo Alto, Calif. The rotorod sampler, an example of a single-stage impactor, reverses the usual process of pulling air through the collector by rotating a collecting rod through the air. Particles are impacted on the collecting-rod face for subsequent examination under a microscope.

³ Sources for wet impingers include MSA midget impinger from Mine Safety Appliances, Pittsburgh, Pa.; Greenburg-Smith impinger from Willson Products Division, Rayovac Co., Reading, Pa.; Unico microimpinger from Union Industrial Equipment Co., Fall River, Mass.; and Gelman midget impinger from Gelman Instrument Co., Ann Arbor, Mich.

with enough force to cause damage. For this reason, multiple-stage or cascade impactors consist of a series of single-stage impactors, each operating at a higher velocity. The largest particles are collected in the first stages during which the velocity through the orifice is the lowest. The smallest particles are collected at the highest velocity in the final stage.⁴

The cyclone typifies centrifugal collectors. A cyclone separator is a structure, without moving parts, that removes particulate matter from gas streams by causing the fluid stream to move in a confined vortex within which inertial forces continuously produce a tangential motion of particles toward the collector wall. The inertial separating force in a cyclone is the radial component of simple centrifugal force. Because of the relative design simplicity, cyclones are inexpensive and can be constructed of materials capable of meeting many temperatures and pressures. Furthermore, cyclones may be designed to handle nearly any dust load or air volume. These factors lead to an extensive application of cyclones, especially when only moderate collection efficiency, 80 percent, is required.

Because of their simplicity of design, cyclones are among the most trouble-free particulate collectors available. Other than erosion and corrosion, plugging of the dust outlet and cake buildup on walls are the two most common operating problems. The former problem can be minimized by proper design, and the latter problem can be minimized by any of several methods, depending on the circumstances. Some of the methods are eliminating condensation through insulation, increasing inlet velocity, electropolishing inner walls, removing pre-cleaners to allow scouring of walls by coarse material, and flushing or grounding.

Cost estimates for cyclones have varied from 7 to 50 cents/cu ft/min of capacity. A typical cyclone of moderate capacity, therefore, costs about 10 cents/cu ft/min uninstalled. Installation costs vary depending on the location. A comparative study of annual operating costs for various dust collectors including power, maintenance, and water (when used), but not amortization, shows for dry cyclones an average of 6 cents/cu ft/min/yr and for wet cyclones 16 cents/cu ft/min/yr. When 10-year amortization is included, the total, average annual costs are, respectively, 8 and 20 cents.⁵

⁴ Sources for such multiple-stage impactors include: Casella cascade impactors from Brinkman Instruments, Inc., Westbury, N.Y.; Unico cascade impactor from Union Industrial Equipment Co., Fall River, Mass.; Anderson sampler from Anderson Samplers, Provo, Utah; and Battelle cascade impactors from Scientific Advances, Inc., Columbus, Ohio.

⁵ Sources of supply for such devices include: Union Industrial Equipment Co., Fall River, Mass.; Zimeny Corp., Monrovia, Calif.; and Mine Safety Appliances Co., Pittsburgh, Pa.

Electrostatic Precipitators.—Air-sampling electrostatic precipitation of airborne particles is useful for collecting relatively large samples with a high collection efficiency for all particle sizes. Electrostatic precipitation is also useful for depositing small-quantity samples with very small particle sizes directly onto an electron-microscope grid. The sampling rate is not affected by the mass loading, or by the total collected material in the sample, and the sample is in a readily recoverable form.

Collection by electrostatic precipitation requires that the particle to be collected have an electrical charge and that it be introduced into an electrical field and directed toward a collecting substrate maintained at a polarity opposite to that of the charged particle.

For cleaning industrial gases by electrostatic precipitation, the high-voltage direct-current corona method of particle charging is universally used. In this process, a high-voltage discharge electrode placed at a proper distance from a grounded electrode ionizes the gas between the electrodes, and current passes through the ionized air. This ionization occurs only in a finite temperature and voltage range, and is dependent on the physical properties of the gas. Below the lower limit of the range there is no current flow, and the upper limit is defined by the dielectric breakdown of the gas when sparking takes place. The rate of ion generation must be sufficient to saturate the field so that the dust particles pass through. The ions attach themselves to the dust particles and these ionized particles are then subject to the electric forces of collection. With sufficient power generation, the corona discharge generates enough ions to accomplish this charging almost instantaneously. When a negative-charge discharge wire is used, a measurable amount of ozone (O_3) is formed. A positive-charge discharge wire system forms very little O_3 . For this reason, positive corona systems are used for space ventilation.

Once the dust particles have been transported to the collector electrode, they must be removed with a minimum of reentrainment during the time the precipitator is operating. For the designer of dry precipitators (collection of dry dust), reentrainment is a very serious problem. Liquid films in wet precipitators self-drain and usually present no reentrainment problem.

Although the fundamentals of electrostatic precipitation are understood, theoretical efficiency is never attained in practice. Thus, despite years of experience, the prediction of precipitator performance is largely empirical. Maintaining the design efficiency in day-in-and-day-out operation is more difficult with precipitators than with many other types of equipment. All of the parameters affecting efficiency—gas volume and density, dust concentration, particle-size distribution, resistivity, gas distribution, and power settings—must be at favorable

design conditions to yield design efficiency. It is not uncommon to find precipitators in apparently normal operation having efficiencies 5 to 10 percent below design efficiency. A precipitator efficiency of 75 to 90 percent, depending on application, is relatively easy to obtain. Above these levels and especially above approximately 98 percent, sectionalization and automatic power controls are necessary.

The purchase cost of precipitators for rates over 400 000 cu ft/min is approximately \$1/cu ft/min. This does not include duct work, dust-handling equipment, or insulation. Total installation costs are quite dependent on the collection efficiency required. Operation cost is the sum of the power cost required for precipitation and the cost required to move the gas through the precipitator. Precipitation power, the major power-cost variable, is dependent on the desired efficiency. Corona power can range up to 500 w/1000 cu ft/min to which the energy conversion efficiency of the power supply must be added. Maintenance requirements for a precipitator installation generally require the service of an engineer or a trained operator in addition to the usual personnel for mechanical maintenance.⁶

Thermal Precipitators.—Thermal precipitators deposit dust particles from a small volume of air onto a surface from which they may be examined, counted, or weighed. Deposition is accomplished by the thermophoresis force that an airborne particle experiences in a temperature gradient. This force causes particles to be driven toward a cold substrate. The thermal precipitator quantitatively collects all particles from the smallest size that can be observed in an electron microscope up to approximately 3 to 5 microns in diameter. Most thermal precipitators operate at a sampling rate of a few centimeters per minute. High-capacity precipitators that sample up to 1 cu ft/min have recently been developed. Costs range from \$300 or \$400 up to \$1,000 per unit.⁷

In Situ Analyzers

The collectors described above employ physical methods of removing particles from the atmosphere and depositing them on suitable substrates for examination, which may involve determining particle concentration, particle mass, or particle composition. In situ analyzers, on the other hand, use physical processes to observe the particles at their positions in the atmosphere. These analyzers are used mainly

⁶ Supply sources of such precipitators include the Bendix Corp., Cincinnati, Ohio; Bell Electronics Corp., Mount Vernon, N.Y.; Mine Safety Appliances Co., Pittsburgh, Pa.; and Gardner Associates, Inc., Schenectady, N.Y.

⁷ Electrical thermal precipitator sources include: Casella standard thermal precipitator, Union Industrial Equipment Co., Fall River, Mass.; Strong-Ficklen thermal precipitator, Joseph B. Strickland, Pasadena, Calif.; and thermopositor, American Instrument Co., Silver Spring, Md.

for determining particle concentration or mass. The composition of particulate contamination is seldom described by the physical means available for in situ analysis. These physical means depend on observation of interaction between a particle and some physical process. Instruments used for air pollution monitoring of particulate contamination in situ are described briefly below.

Photometric Analysis.—The dimensions of airborne particles are usually within an order of magnitude of the wavelength of the light used to illuminate them. When a particle is illuminated with a beam of light, the amount of light scattered by that particle varies roughly with the projected area of the particle. By causing particles to pass singly through a light beam, it is possible to collect pulses of light scattered by each particle at a particular angle, analyze the total light flux in each pulse, and obtain a particle-size distribution from the individual particles.

Alternatively, an aerosol photometer collects the light scattered from a volume of aerosols containing many particles and produces data that indicate the total area of all the particles in the volume of gas. By careful optical design, it is possible to measure light transmission through the aerosol; for example, no scattered light is permitted to enter the collecting optics. This means that all the undeviated light in the beam transmitted through the suspension and none of the scattered light reaches the collecting optics.

To summarize, the photometer is used to determine the total number of particles in a given volume of aerosol. The light-scattering, single-particle counter describes the particle-size distribution by the number of particles in a given volume of aerosol.

Light-scattering, single-particle counters detect single particles of at least 2/10 micron. Scattering angles approaching 90° are used. Concentration up to 1 million particles/cu ft can be analyzed without significant coincidence. Costs range from approximately \$3,000 to \$20,000, depending on desired accessories.⁸

An extinction meter indicates the total number of particles in a given volume of aerosol. The extinction meter can be used with an artificial light source to determine the concentration of particles in a given volume of aerosol, or the Sun can be used as a light source to determine atmospheric turbidity or plume transmittance from an emitting air pollution source. Plume transmittance can be obtained by the photometer sighting a pair of contrasting targets, one through and the other clear of the plume.

⁸ Sources of supply include the Royco Instrument Co., Menlo Park, Calif.; Bausch & Lomb, Inc., Rochester, N.Y.; Particle Technology, Inc., Sunnyvale, Calif.; and Climet, Inc., Sunnyvale, Calif.

Typical optical device costs range from \$1,000 up.⁹

In recent years high-power laser systems and high-sensitivity photometers have made it possible to collect light scattered back from discrete aerosol clouds at long distances. These devices involve a pulse-laser system producing a collimated beam and viewing optics, also collimated, to intersect the laser beam at a given distance within the aerosol cloud. The amount of light scattered back from the aerosol into the receiving optics gives an indication of the concentration of particles within the aerosol cloud at the intersection of the laser beam and the axis of the receiving optics.

No commercial devices of this type are presently available. Experimental systems have been investigated primarily under Government sponsorship and show great promise for remote detection and analysis of aerosol clouds.

Condensation Nuclei Counters.—If submicron aerosol particles are injected into a volume in which the relative humidity is near saturation or supersaturation with respect to liquid water, the vapor in the environment condenses on the particles and produces droplets that can be easily seen with simple optical systems. The submicron particles act as heterogeneous condensation nuclei. By controlling the degree of supersaturation, the sizes of particles activated to nucleate the water vapor can be selected. This phenomenon also occurs with gas-molecule clusters, such as SO_2 , SO_3 , and NH_3 . Such gas molecules are commonly present in environments in which air pollution occurs. Thus, the number of activated nuclei is in direct relation to the total level of particulate pollution present in the environment.

It is possible to achieve the required supersaturation by adiabatic expansion of a compressed air sample. The droplets that form when the air sample is expanded are viewed with a light-extinction meter. The concentration of droplets is directly proportional to the amount of light obscured. The concentration of droplets is also directly equivalent to the total concentration of nuclei.¹⁰

Experimental systems.—The aerosol analyzing systems described above are generally available commercially. In addition to these sys-

⁹ Such devices include the Brice-Phoenix photometer from Phoenix Instrument Co., Philadelphia, Pa.; Aminco angular scattering photometer from American Instrument Co., Silver Spring, Md.; Royco aerosol photometer from Royco Instrument Co., Menlo Park, Calif.; Leitz Tyndalloscope from Ernst-Leitz, Inc., New York; Sinclair-Phoenix photometer from Phoenix Instrument Co., Philadelphia, Pa.; and the particle detection unit from T-D Associates, Baltimore, Md.

¹⁰ Two commercial sources for condensation nuclei counters are General Electric Co., Schenectady, N.Y., and Singco Associates, a division of Bolt, Beranek and Newman, Cambridge, Mass.

tems, however, several other systems in various stages of development apply physical principles. These include:

(1) *Spectral emission*.—If aerosol particles are passed through a flame or through a plasma, the particles are vaporized, heated to incandescence, and the light pulse of a particular wavelength is emitted. This light pulse can be analyzed on a suitable spectrophotometer for both concentration and composition. It is possible to detect particles as small as 0.1 micron.

(2) *Electrical mobility*.—Small particles can be charged unipolarly and their mobility determined by measuring their collection in a given electrical field. Single-electron charging of submicron particles, combined with current measurement, gives data on total quantity of submicron particles. Saturation charging of larger particles and current collection in any preset field give mobility data (ref. 19).

(3) *Acoustical techniques*.—If particles in air are passed through a sensor in which they are gradually accelerated to about 100 m/sec and suddenly projected into a wide hexacavity, the particles produce a pressure pulse that results in an audible click (ref. 20).

(4) If particles are removed from an airstream by a probe that is connected to the grid of an electrometer, the electrical charge of each particle normally produces a significant deflection in the electrometer reading (ref. 21).

This review of new experimental systems is by no means complete. One-of-a-kind prototypes of such systems are being evaluated. Additional concepts indicate the variety of physical phenomena that can be used to detect particles in the ambient air.

Emission-Source Analysis

Essentially all of the collection devices described in the previous section can be used with certain precautions for stacks and other emission sources.

In many municipal ordinances, allowable emissions from process vents or from power plant stacks are limited in terms of plume opacity. Opacity may be estimated by visually scanning the plume against the sky background with or without a comparison chart. The opacity of the plume can also be determined by photometric observation across a fixed distance within the stack or vent itself. A light source and photometer, acting as an extinction meter, are used. It is necessary, however, that precautions be taken to insure that deposits on the lens system of the light source and extinction meter are eliminated or prevented. A stream of clean air across the lens system is often adequate.

In addition to the optical visibility limitations, many stack emissions are limited in terms of the mass of particles that can be emitted

per unit volume of gas or, in terms of the mass that can be emitted, per unit weight of input process material or per unit of power generated. The mass of emitted material is determined as a function of gas flow or of time. The gas velocity within the stack is measured, usually with a pitot tube, to insure isokinetic sampling. An isokinetic sample probe is inserted and is traversed across the stack. Materials are collected on a suitable filter medium or in wet or dry collectors, considering the temperature and dew point of the gases in the stack. Usually, manual methods are used to collect the sample and to adjust sample velocity to insure isokinetic sampling. In the last few years, however, modifications of this technique have been developed. In some systems the sample particles are collected on a suitable filter tape, and the mass of particles per unit area of filter tape (correlative to unit volume samples) is determined by beta-ray transmission (ref. 22).

In addition to these essentially standard techniques, a number of one-of-a-kind developments have been reported; for example, triboelectric measurements of charge deposited on a collecting cone grounded through an electrometer depend on the quantity of charge particles impacting on the cone.

In general, measuring stack or emission pollutants requires the same types of devices as ambient-air monitoring. Isokinetic sampling must be carried out within the stack, and the sample system must not be affected by the high temperature and/or high dew point of water or acid gases within the stack. Corrections for temperature and gas compositions must be included, because combustion products with densities other than that of air may be present.

NASA Contributions to the Art

SPACECRAFT-CABIN ATMOSPHERE MONITORS

A spacecraft cabin is a closed ecologic environment, and that a nontoxic atmosphere must be maintained within the cabin is a requisite for manned spaceflight. The National Aeronautics and Space Administration has, therefore, invested a great deal of effort in identifying, measuring, and controlling the components of a sealed-spacecraft-cabin atmosphere. Much of this investment has been channeled into the design and production of monitoring equipment, and some of this equipment is functionally suited to air pollution monitoring on a broader scale. NASA developments in monitoring devices that represent novel or improved features applicable to air pollution monitoring have been selected for review here.

Tests with unmanned and manned cabin simulators have shown that nearly 150 vapors are generated in a closed system (ref. 23). These vapors, some of them potentially toxic, are primarily produced by three sources: (1) the metabolic processes of the crew, (2) the supplies and food stored for the use of the crew, and (3) the operation of the spacecraft systems (refs. 24 and 25). Additional sources are the materials of which the cabin is constructed (ref. 26) and the reactions of products from other sources. The studies that have been conducted to identify and measure these contaminants utilized commercially available analytical instrumentation, such as gas chromatographs, infrared spectrometers, mass spectrometers, and biological sampling devices (refs. 27, 28, and 29). This instrumentation has also been used for laboratory analysis in air pollution studies. However, the emphasis in air pollution instrumentation is shifting toward portability, durability, and simplicity of operation (manual or automatic). The development of flight-rated instrumentation by the National Aeronautics and Space Administration has achieved some of the goals of air pollution investigators. Eight NASA-developed instruments originally designed for cabin monitoring, which we feel are of interest to the field of air pollution, are described in detail below.

Small General Purpose Cycloidal-Focusing Mass Spectrometer

The NASA Flight Research Center at Edwards Air Force Base, Calif., developed this mass spectrometer (refs. 30 through 33) in response to a need for a flight-rated monitor for respiratory gases. The original use of the instrument was to monitor continuously the respiration of a test pilot for correlation of quantities of various respiration products with stress conditions being undergone by the pilot.

The mass spectrometer monitors vapors with molecular weights of 3 to 100 atomic mass units (amu) (fig. 1). For flight operation, 12 gases are monitored simultaneously with a continuous input. The delay time (determined by input system) is 300 milliseconds, and the instrument response time is 30 to 50 milliseconds. The accuracy of measurement varies with the concentration of gases monitored. For high concentrations, the accuracy is ± 3.5 percent of full scale, ranging to ± 50 percent for low concentrations of 600 ppm.

This compact instrument is 10 by 11 by 11 inches and weighs 28 pounds, exclusive of the vacuum system. It has a high reliability rating. Tests at the Flight Research Center have shown that zero drift is approximately 1 percent in 6 months, and that output with a constant input varies ± 2.5 percent. The instrument has an automatic calibration circuit that recalibrates every 2 minutes. The life of the ion source is approximately 250 hours, and the solid state electronic circuitry has a life expectancy measured in years.

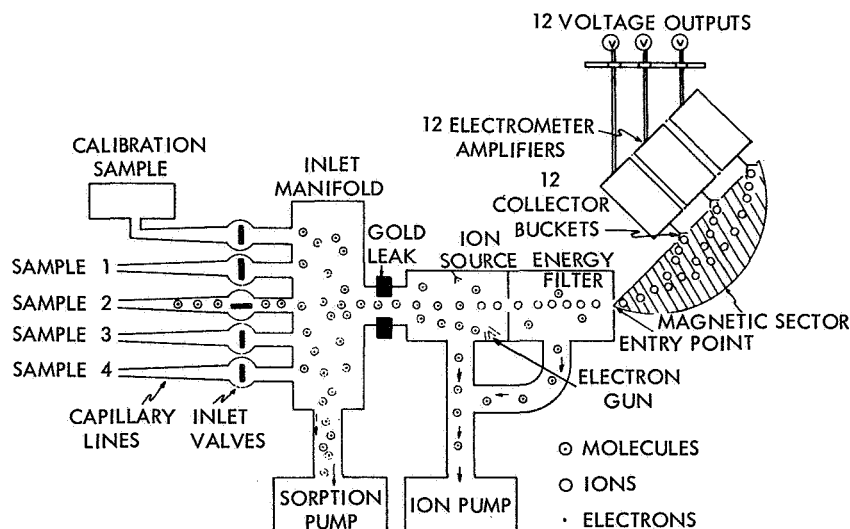


FIGURE 1.—Schematic diagram of operation of cycloidal focusing mass spectrometer.

This instrument is suitable in its present form for use as an air pollution monitor for gases within the 3- to 100-amu range. Because of its small size and durability, it can be used in any type of vehicle as well as in a stationary location. There are no commercially available mass spectrometers that meet the size and performance specifications of this device. No additional developmental costs would be required for using this instrument in air pollution monitoring. The estimated cost of the instrument, \$50 000, is difficult to justify for an enforcement agency but would be acceptable for a research group.

Nonmagnetic Flight Mass Spectrometer

This flight-weight monopole mass spectrometer (refs. 33 and 34) was developed by the General Electric Co., Apollo Systems Department, Daytona Beach, Fla., for the NASA George C. Marshall Space Flight Center. The developers took a commercial GE Monopole 600 partial-pressure analyzer and made it smaller and more rugged and reduced its power requirement, thus designing a feasibility model for instrumentation to be flown in Saturn launch vehicles. Three applications were sought:

- (1) Detecting hydrogen, oxygen, and hazardous-gas mixtures from gas systems and monitoring light atmospheric gas constituents with mass ranges of 2 to 50 amu.
- (2) Measuring ambient atmospheric constituents, hydrocarbon fuels, toxic gases, products of offgassing, and so forth, with mass ranges 2 to 300 amu.
- (3) Detecting heavier hydrocarbon contaminants and toxic gases with mass ranges 2 to 600 amu.

The development and testing thus far has been restricted to the 2- to 300-amu range. However, the instrument as designed is capable of detecting materials with mass unit numbers up to 600. Sensitivity is high—partial-pressure measurements can be made up to 10^{-10} torr. The instrument provides unit resolutions over the entire mass range with a scan rate of 60 seconds for the entire range. Manual scan is also provided. The output is suitable for driving a 0- to 5-volt recorder. Peak position on the recorder shows mass number, and peak height indicates quantity at that number.

This instrument is nonmagnetic. The samples are drawn through a small leak into the ion-source section where the atoms and molecules are ionized. Ion separation is performed by a combined radiofrequency (rf) and direct-current (dc) field. Under any given set of applied voltages, only ions of one mass stream to the end plate of the chamber. These pass through an aperture and strike the first stage of an electron multiplier. The rf and dc voltages can be systematically varied to cover a desired range of ion masses. Monitoring

these voltages provides, then, a measure of the mass at any given moment. A plot of mass number versus partial pressure can then be used to identify the chemical nature of the constituents of the sample drawn into the tube. After the initial analysis, succeeding identifications can be partially automated.

The instrument's dimensions are 8 by 6 by 16 inches, and it weighs 16.8 pounds, exclusive of a vacuum system. Power requirement is less than 30 watts. Because this device was developed as a feasibility study, the commercial quality and reliability requirements were not considered, but an operating flight unit would be required to meet standards and procedures such as MSFC-FTB-154. The feasibility study demonstrated that these requirements could, in fact, be met by a flight unit designed according to this prototype.

An instrument built to the specifications of this prototype would be suitable for detection and analysis of the gaseous constituents of the atmosphere with mass numbers in the range of 2 to 600 amu. Although the gas sampling rate is very, very low—a fraction of a cubic centimeter per second, the large number of molecules that can be analyzed in a relatively short time for both composition and concentration makes the device useful for atmospheric problems. Both the GE Monopole 600 and the Consolidated Electrodynamics Corp. analytical mass spectrometer perform essentially the same functions. However, both are several orders of magnitude larger and require considerably more power. The modified instrument is admirably suited for mobile use, and its relatively low estimated manufacturing cost of \$15,000 makes it attractive for civic and research groups. The estimate for design, checkout, and field testing for a production device is approximately 3 man-years of effort.

Trace-Gas Analysis Procedures

In 1966 the National Aeronautics and Space Administration and the Air Force School of Aerospace Medicine jointly conducted a series of experiments on contaminants in a closed ecologic environment. Aerojet-General (refs. 35 and 36) was under contract to the Air Force to perform analytical analyses of the contaminants, and they developed procedures for collecting and analyzing the gases. Personnel from Aerojet-General, working with a NASA team and Southern Research Institute personnel, are continuing the development of this procedure at the John F. Kennedy Space Center to analyze contaminants off-gassed by materials and systems used in the Apollo cabin.

This procedure represents a well-defined, highly reliable technique for the use of commercially available equipment in an application intimately related to air pollution research. The salient features of this procedure are in sample treatment and data handling. Analytical

systems used are gas chromatography and mass spectrometry with commercially available equipment. The procedure permits analysis of some 100 compounds contained in samples from the Apollo cabin in approximately 90 minutes, although manual planimetry of chromatograms now requires more time. The procedure is as follows:

A sample is taken by cryogenically fractionating the spacecraft-cabin effluent by freezeout at 0° C, -78° C, and -175° C. Each of the three fractionated samples is passed, in turn, through four chromatographic columns, the packing material in each column having been selected to obtain maximum separation of the compounds with slightly different fractionalities. The gas-flow system is arranged to direct samples to the mass spectrometer either from the fractionated sample bottles or from one of the gas chromatographic columns.

The method has demonstrated high reliability for a large number of samples but highly skilled personnel are required to maintain this level of reliability. Thus, the possibility of transferring this technique to an automated or routine laboratory analysis is remote.

This system is specifically designed for repetitive analysis of gas samples that may contain hazardous materials. In the field of air pollution it would be most suitable for monitoring special manufacturing processes or in research work. If the gas chromatographic and mass spectroscopic equipment is available, the gas-handling system and cryogenic storage facility would cost approximately \$5000. Although variations on this procedure exist in many analytical laboratories, there are no commercial systems of this nature. The proven reliability and the documentation of this system recommend its use to air-pollution-research facilities.

Colorimetric Glycol Detector

This device is a specific detector for glycol vapor and is to be used in spacecraft-cabin atmospheres.

The glycol detector is currently in the developmental stage, and its limits of operation are being sought at the NASA Manned Spacecraft Center. At this time the device seems sensitive to 1 ppm of glycol vapor. Interferences with other materials are being investigated. About 40 have already been tested, including alcohols, ketones, esters, and aldehydes. Formaldehyde produces the same reaction (color) as glycol does, and the other aldehydes (acetaldehyde, butyraldehyde, and so forth) produce different colors. The other materials tested have no effect on the detector.

The detector consists of a glass tube 6½ inches in length and ¼ inch in diameter (fig. 2). The interior is divided into three reagent sections by porous spacers. The first section contains periodic acid (HIO_4), the second contains catechol dimethyl ether, and the third contains H_2SO_4 stored on fused silica gel. The tube is sealed after being packed with

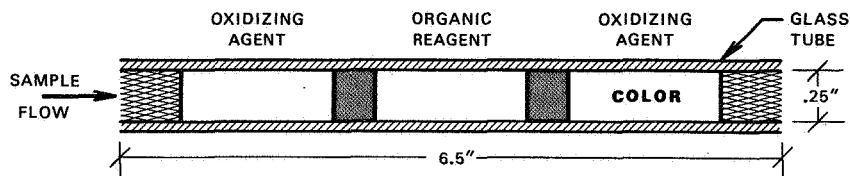


FIGURE 2.—Colorimetric glycol detector.

these reagents, and the ends are opened for use. If glycol is present in the sample introduced into an open tube, the HIO_4 acts as an oxidizing agent and produces an aldehyde. The aldehyde is condensed by the organic reagent in the second section to a methylene compound, which in turn is oxidized in the third section to produce a color—the intensity of which is proportional to the concentration of glycol in the sample.

No reliability has been established for this device because it is still experimental. Proper sealing is necessary, because atmospheric moisture collected on the silica gel in the last section will degrade operation. Storage life and shelf life are expected to exceed 12 months.

This device is designed only for detection of glycol vapors with manual use. The cost is very low, approximately \$1 for each detector. Sampling costs are also low, because a real-time indication of the presence or absence of glycol is obtained during the sampling process. Other colorimetric detectors exist, such as the Kitagawa precision gas detector marketed by the Union Industrial Corp. and the Universal testing kit sold by the Mine Safety Appliances Corp. However, neither is specific for glycol. The glycol detector represents a device suitable for detection and analysis of glycol in the atmosphere at a very low per sample cost (the development of a production item would require about a $\frac{1}{2}$ -man-year effort).

The principle utilized suggests two other possible applications:

- (1). Use of the operating principles of sensitization, reaction, and indication in tubes specific for vapors other than glycol.
- (2). Production of an automated device using these operating principles. It appears at least feasible that tapes could be manufactured in a process analogous to that used in producing Polaroid film and used with a filtered tape-air sampler for continuous monitoring (ref. 37).

Hot-Wire Detector for Chemically Active Materials

A hot-wire detector for chemically active materials (ref. 38) used in gas chromatography was developed at the NASA Manned Spacecraft Center. Gas chromatography, as used for cabin-contaminant identification and analysis, has been limited because the filament in available hot-filament detectors reacted with certain gases and vapors.

Thus, only materials that did not react with the filament could be measured.

The new detector can measure gases and vapors that are reactive with the detector filament. The filament is designed to change its electrical resistance as a function of the effluent composition when it reacts chemically with the effluent vapors in the gas chromatographic apparatus.

A titanium or zirconium filament is used for analysis of vapors that are evolved at high temperatures. Other reactive metals may be used for vapors that are evolved at low temperatures. Before sample introduction an inert gas such as helium is passed at a controlled rate over the filament that is heated to the desired operating temperature by a constant-current source. When equilibrium is reached, the electrical resistance of the filament is measured. The sample is then introduced, and the resultant resistance change of the filament with time is measured and plotted on a chromatogram. The quantity of each component in the sample is determined, as in conventional gas chromatography, by measuring peak heights on the chromatogram and multiplying by calibration factors. Because the filament is chemically reactive, its characteristics change, and frequent recalibration is necessary.

Microwave Spectroscopy

For several years the NASA Langley Research Center has been developing microwave spectroscopy into a tool for gas analysis of trace contaminants (refs. 39 through 47). Several years ago, Langley personnel built a microwave spectrometer, but now use a commercially available device manufactured by the Hewlett-Packard Co. The techniques developed at Langley regarding the theory and use of microwave spectroscopy are of prime interest in air pollution monitoring.

Microwave spectroscopy is an analytical technique similar to mass spectroscopy and has several potential advantages. Highly specific identifications can be made by measuring the frequencies of the microwave absorption lines of molecules. Compounds may be unambiguously identified, even in mixtures. Molecules are not fractured by ionization (as in mass spectroscopy) nor is a carrier gas needed (as in gas chromatography). Because the technique is all electronic, it is very amenable to automation.

Detection of molecules is based on the absorption of various microwave wavelengths by different gases. Only polar molecules absorb microwave energy, so nonpolar gases and vapors such as methane, benzene, nitrogen (N_2), and carbon tetrachloride (CCl_4) cannot be detected by this method. The average number of lines in the absorption spectrum of a polar molecule is 400. The number indicates highly unique spectra, and this uniqueness, combined with high-resolution

and highly accurate frequency measurements of the microwave spectrometer, usually permits identification of a gas by measurement of only a few of the 400 lines.

The Langley Research Center program is concerned with establishing useful standards for microwave spectroscopy. Mississippi State University is cataloging spectral lines under a NASA grant. A computer-operated spectrometer will soon be used to generate identification spectra for a large number of compounds, and Langley is currently discussing the maintenance of these spectra by the National Bureau of Standards. Work is also being done in the development of a dual-resonance microwave spectrometer that will have even greater precision in identifying the components of a mixture and in establishing techniques that can be used to make quantitative measurement more accurate.

Langley Research Center is leading the development and application of this relatively new analytical technique. Microwave spectroscopy should prove to be a valuable tool for air pollution control centers and laboratories. Because of the cost and size of the equipment (comparable to commercial mass spectrometers), this technique is definitely laboratory oriented.

NASA's work in this area is well documented. More extensive treatments of the theory and use of microwave spectroscopy can be obtained from the references that are noted above and are listed at the end of this report.

Contaminant Sensor

A laboratory prototype of a contaminant sensor (ref. 48) was developed by Perkin-Elmer under contract to NASA Langley Research Center. This prototype is suitable for adaptation to a flight instrument to be used in a spacecraft cabin for continuous monitoring of the atmosphere.

The prototype contaminant sensor was built and tested with samples of known gases and unknown mixtures. Concentrations in the range of 0.5 to 5 ppm can be detected, and concentrations over 100 ppm can be quantitatively determined.

This device consists of a mass spectrometer coupled with an accumulator cell containing a sorbent material on which the contaminants from the air are concentrated. Contaminants collected in the accumulator cell at room temperature are subsequently desorbed by heating the cell or by a vacuum system and are passed to the inlet system of the mass spectrometer. An initial precut removes residual air from the accumulator cell to provide pressures compatible with the mass spectrometer input leak and to increase the relative concentration of the contaminants.

The mass spectrometer used in this sensor is a CEC 21-614-1 with a scan range of 2 to 200 amu, and is available commercially. The collection system is the novel portion of this instrument. The system has three accumulator cells, each containing a different sorbent so that a wide range of contaminants could be recovered. Each cell has a Teflon-lined steel tube $\frac{3}{8}$ inch in diameter. The sorbents used were Porapak Q, charcoal, and molecular sieve no. 5.

The techniques used in the contaminant sensor are applicable to air-pollution-monitoring stations. A wide range of contaminants can be collected and measured, which is useful for laboratory applications.

Photoionization Source for a Mass Spectrometer

This instrument was developed by the GCA Corp. for the Langley Research Center (ref. 49). After the prototype instrument was made and tested, certain limitations were found in its discrimination between ions with differing ionization potentials and coinciding mass numbers, for example, CO and N₂. The instrument was modified by using an argon filter that reduces scattering and the higher order ultraviolet spectra. The modified instrument is capable of detecting CO and N₂ to a lower limit of 100 ppm.

This instrument differs from other mass spectrometers in the method by which the atoms or molecules to be analyzed are ionized. The usual technique is bombardment by electrons or ions. This instrument ionizes the particles with ultraviolet light. Although ionization is slower this way, much less dissociation of complex molecules results in simpler spectra and an easier determination of the composition of gas mixtures containing high-molecular-weight gases.

The instrument can detect gas traces in the 10- to 100-ppm range. Work to date has indicated that detection in the 1-ppm range should be possible with this technique, and that an automated scan of the 2- to 50-amu range would take about 5 minutes for this degree of precision.

The applicability of this device to air pollution monitoring is tenuous at present, because only one prototype instrument has been produced. However, the technique appears promising for use in laboratory analysis. The possibility of ionizing high-molecular-weight gases without extensive fragmentation indicates specific applicability to analysis of photochemical smog, hydrocarbons, and so forth.

HAZARDOUS-GAS AND TRACE-GAS ANALYSIS

The identification and analysis of possible toxic concentrations of gases and vapors within a spacecraft cabin are not the only areas of gas monitoring of interest to the National Aeronautics and Space

Administration (refs. 50, 51, and 52). Several other aerospace systems require analytical work with gases. These include:

(1) *Leak detection*.—The detection of leaks in storage vessels, transfer lines, and spacecraft is highly important when hazardous fuels are used. For instance, hydrogen is highly combustible, and a leak in an enclosed space, such as the interstage area of a spacecraft, must be detected before an explosive concentration is reached.

(2) *Purity tests*.—Gases used in certain aerospace applications, such as fuels and low-friction gas bearings, must have a high degree of purity; and highly sensitive analytical methods are required.

(3) *Trace-gas analysis*.—The products offgassed from a pyrolyzing surface, such as an ablative heat shield, can be used to give insight into its mode of decomposition and hence provide a measure of its utility.

The National Aeronautics and Space Administration has developed and sponsored the development of novel and improved techniques of gas analysis toward these ends. As in the case of cabin-atmosphere monitoring, some of these techniques have applicability to the monitoring of gaseous air pollutants, and we describe such developments in detail below.

Gas Chromatograph to Mass Spectrometer Transfer System

This system was developed at the NASA Ames Research Center by Dr. John Parker and Marius Kendall. They were studying ablative heat shields for reentry vehicles, and required a method of analyzing the material offgassed as the shield pyrolyzes. Standard analytical techniques call for the use of infrared spectroscopy, gas chromatography, and mass spectroscopy. Shield materials are pyrolyzed in helium in specific time increments and the offgassed products sampled with a pyrolysis sampler. The same sample should be run in both a gas chromatograph for high resolution and a mass spectrometer for high speed.

Coupling of commercially available gas chromatographic and mass spectroscopic equipment is the unique feature of the system developed at Ames. The gas-transfer chamber of the system takes the gases that are separated by the gas chromatograph and delivers them to the mass spectrometer in a continuous operation. There is also a provision for transfer to an infrared spectrometer. The chamber is a molecular separator and removes 95 percent of the helium carrier gas with a loss of only 5 percent of the sample gases. The gas chromatograph provides readout on strip chart and magnetic tape, and the mass spectrometer reads out on oscilloscope and strip chart. A computer program for reduction of data recorded on magnetic tape has also been generated at Ames.

Similar procedures are used in several laboratories engaged in gas analysis, including some doing air pollution research. The transfer mechanisms used are "home built" by each laboratory, and comparison with the Ames device is difficult. However, the high efficiency, reliability, and record of use speak well for the Ames procedure. It is not applicable to remote or mobile monitoring, but provides improved laboratory capability for air pollution research. The cost of the entire system used by Ames is \$80 000, but the transfer mechanism alone would cost only about \$2 000.

Technique for Measuring Nitrogen in Argon

This technique, developed for the NASA Kennedy Space Center, permits the measurement of nitrogen in argon gas in the parts-per-million range (ref. 53). NASA required such a technique because of the need for ultrapure argon as a welding gas, an inert atmosphere gas, and so forth. The technique is also applicable to detection of nitrogen in oxygen.

The technique requires material and equipment usually available in a gas-analysis laboratory and permits accurate measurements in a wide sensitivity range with only a small sample. Two gas-sampling chambers, a molecular sieve column, and a thermal-conductivity detector cell are used. The two chambers, arranged in series, are purged with a common carrier gas into the molecular sieve column that elutes into the detector cell. Gas samples to be analyzed are injected into a chamber (using a 30-cc sample) to determine concentrations of 5 ppm and up or the second chamber (using larger size samples) to determine concentrations in the parts-per-billion range. Determinations are made with a standard gas chromatographic column and a thermocouple detector.

The inherent reliability of this technique is limited only by the skill of the personnel who carry out the necessary manipulations. NASA has no plans to automate the procedure.

Because this system is designed for the analysis of trace gases in a single-component high-purity carrier gas, it is not applicable to general air pollution monitoring. However, in some instances a stack-gas analysis problem occurs in which only two components are present; in this case, the procedure might be suitably modified. The relatively low cost (approximately \$500 for the sampling chambers and controls, exclusive of the gas chromatographic and detection systems) for implementation of this procedure would make it worthwhile for simple or easily definable two-gas systems.

Hydrogen-Gas-Detection System

This instrument system, which was developed at the Kennedy Space Center, permits continuous, electrical monitoring from a remote loca-

tion (ref. 54). The areas monitored are potential gaseous hydrogen (H_2) leak points in liquid and gaseous H_2 transfer and storage areas, launch-pad towers, and pad aprons. Continuous atmospheric sampling is accomplished by air diffusion through the perforated cover and convection through the heated elements in the detector. The bridge output signal is a function of the amount of combustible gaseous H_2 in the atmosphere being sampled over a range of 0.5 to 4.0 percent in air, and is produced by an amount of gaseous H_2 in excess of a predetermined level (1 percent), actuating an alarm circuit at the control module and display panel.

The system consists of a commercially developed detector (sensor), a control module (General Monitors, Inc., model M135), and related alarm-transmission equipment and display panels. The detector head is basically two legs of a Wheatstone bridge; one leg provides the environmental temperature reference, and the other leg is covered with a H_2 -sensitive catalyst. The control module provides individual control and readout for its detector; contains adjustment circuitry for setting parameters, a meter for measuring the percentage of H_2 gas concentration, and an alarm lamp for indicating when a specific H_2 concentration is exceeded. The display panel contains an alarm-condition lamp and confidence indicator (to monitor the excitation current to the detector). A self-test capability verifies that the detector is operable by electrically simulating a hazard condition at the detector.

The system has been in continuous use for more than a year at the Kennedy Space Center, and no serious difficulties have occurred. This is indicative of a high degree of system and equipment reliability.

This instrument system was specifically designed for the detection of H_2 in air; however, it is adaptable (with proper catalyst selection) for detecting any combustible gas. At a cost of less than \$500 per complete module, it is eminently suited for use in both industrial hygiene and air-pollution-monitoring systems (especially when storage facilities for combustible gases and/or vaporized liquids exist).¹

Other similar devices use platinum catalyst detectors for all combustible gases. With the proper catalyst selection, several combustible

¹ Similar devices are on the market. The Erdco Engineering Co. produces a combustible gas detector, using a platinum-coated catalyst as an element in a Wheatstone bridge circuit to detect combustible gases; the Mine Safety Appliances Co. produces a combustible gas indicator, using a platinum filament as one element in a Wheatstone bridge circuit for indicating explosive and combustible limits of gases; the Teledyne Inc. produces a series 100 combustible analyzer, using catalytic combustion on a heated platinum filament as a detector for combustible gases in process streams; and the Davis Instruments produces a model 11-3400 portable combustion detector, using a coiled platinum filament as one element of a Wheatstone bridge circuit and reading out any imbalance as percent combustible gas.

gases could be monitored, and the concentration level of each gas could be obtained on a readout meter.

Hazardous-Gas-Sampling System

This sampling system, developed by John Barnes at the Marshall Space Flight Center, has been installed at launch pads at Cape Kennedy. It provides multipoint sampling for the detection of leaks in any fuel or gas system in the interstage areas of Saturn rockets. Because of the large volumes involved, several points must be monitored to determine concentrations of hazardous gases or vapors before explosive levels are reached.

Monitoring is done with a commercially available Consolidated Electrodynamics Corp. residual gas analyzer. Only tubing and sampling orifices are within the spacecraft; the rest of the analyzer is outside, approximately 500 feet from the sampling locations. The 1/4-inch stainless steel tubing runs through the umbilical cable to the sampling orifices in the interstage area and is disconnected just prior to launch. The purpose of having most of the monitoring equipment outside the spacecraft is to minimize size and weight problems in the spacecraft.

A valve sequencer, operated by a computer, is used to collect gas from each orifice in succession. The four hazardous gases to be detected are H_2 , O_2 , monomethylhydrazine (CH_3NHNH_2) vapor, and nitrogen tetroxide (N_2O_4) vapor. Because only these four gases are of interest, an automatic peak selector rather than a spectrum scan is used. The coupling device on the tubing at the umbilical disconnect point restricts gas flow, so response time is approximately 50 seconds. The gold leak detector of the CEC mass spectrometer cannot be used in this system because the oil-pumped vacuum system of this detector introduces too much dirt into the lines. The gold leak has been replaced by a Granville-Phillips servocontrolled capillary, which regulates gas flow as a function of pressure.

This system has been very reliable and has survived launch conditions in its protected position under the launch pad. Continuous monitoring has been performed for periods in excess of 24 hours. The system is not sensitive to low concentrations in the parts-per-million range, the lower level of sensitivity being about 0.1 percent.

The cost of the system, exclusive of the computer and the mass spectrometer, is approximately \$20 000. As an air pollution monitor it would be best suited for fixed-station monitoring, such as stack-gas monitoring, in an industrial process system. Remotely located instrumentation in a fixed installation provides a new approach to monitoring inaccessible locations.

Gaseous Hydrocarbon Monitor

This instrument was developed by the IIT Research Institute for the Marshall Space Flight Center to detect gaseous hydrocarbons (refs. 55 through 58). It was developed to sample gaseous systems rapidly (air, nitrogen (N_2), O_2 , and helium (He)) used in Saturn and other spacecraft for life-support systems and for gas-lubricated bearings. Traces of hydrocarbons in O_2 systems could introduce chemical-reaction hazards, and hydrocarbons in a gas used for bearing lubrication could condense, increase friction, and impair the performance of the guidance system.

The gaseous hydrocarbon monitor is based on chromatographic separation and determination by flame ionization (fig. 3). It automatically samples gas at a variety of pressures and separates all hydrocarbon constituents, in a specially packed short chromatographic column. Each hydrocarbon is introduced into a flame-ionization detector, and the detector's output is integrated and recorded by digital methods.

This instrument is calibrated for heavy hydrocarbons—heavier than $C_{14}Hn$ —by using a known mixture of heavy hydrocarbons as a reference standard and for light hydrocarbons by using hexane as a reference standard. The lower limit of detection of hydrocarbons in gaseous systems is approximately 0.05 ppm (by weight).

This instrumental procedure replaces the standard analytical method of bubbling the gas through a solvent, evaporating it, and analyzing it with infrared spectroscopy. It greatly reduces the time required for analysis—each analysis taking 60 to 80 seconds—and increases sampling frequency.

This instrument would be useful for air pollution research in determining hydrocarbon content in air from automobile and aircraft exhausts and industrial production. It is not suited for mobile use, but would be a useful research tool.

Hydrogen Detector

This instrument is used as a portable detector for hydrogen in air, oxygen, nitrogen, or helium in the atmosphere or in gas supply systems (ref. 59).

The sniffer is a portable monitor that indicates the presence of H_2 in contact with activated palladium black by a change in color of a thermochromic paint and indicates the quantity of H_2 present by means of a sensor probe and continuous readout.

It consists of a short, thin-walled glass or metal tube, packed with 0.5 gram of powdered, activated palladium black held in place with compressed glass fibers (fig. 4). The outside of the tube adjacent to the palladium black is coated with a thermochromic paint having two

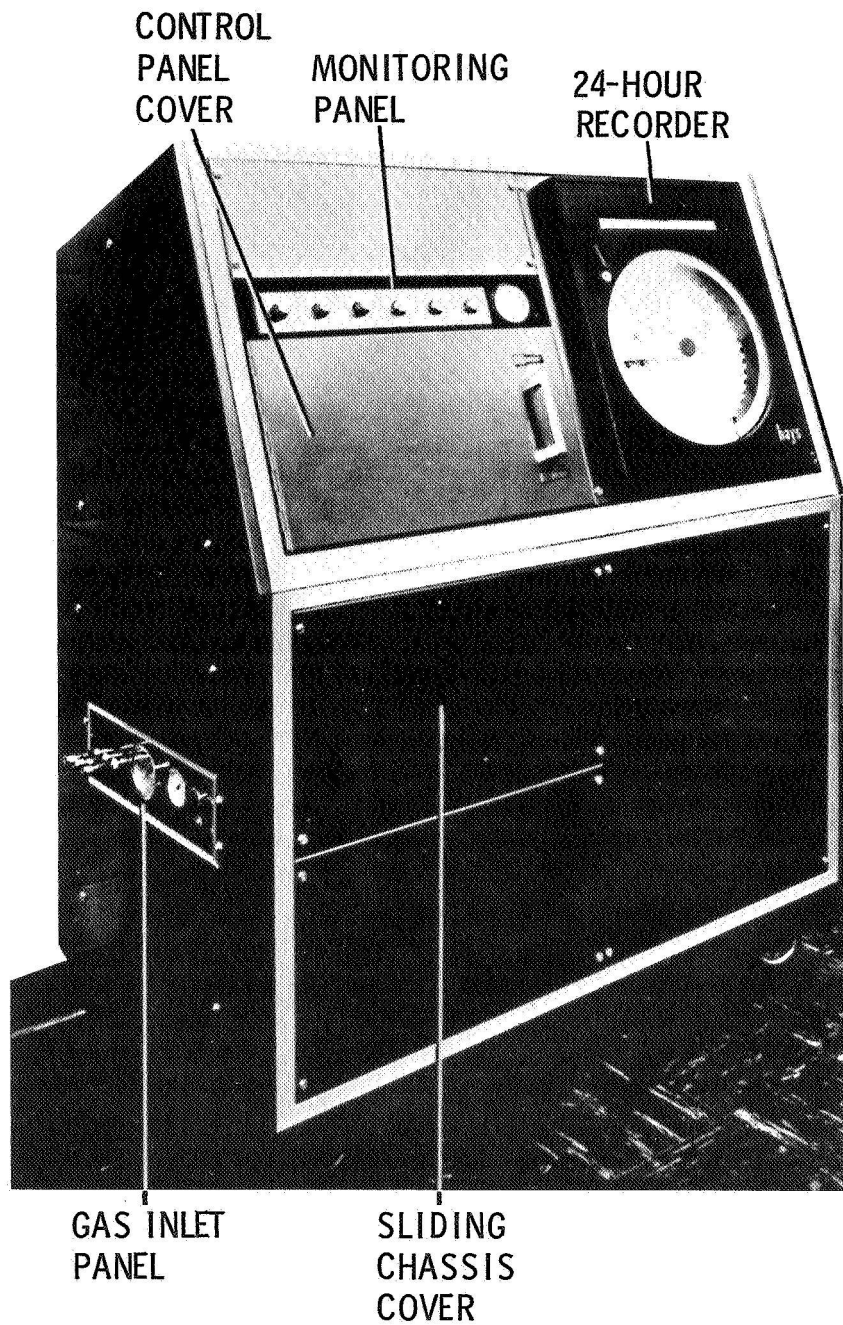


FIGURE 3.—Gaseous hydrocarbon monitor.

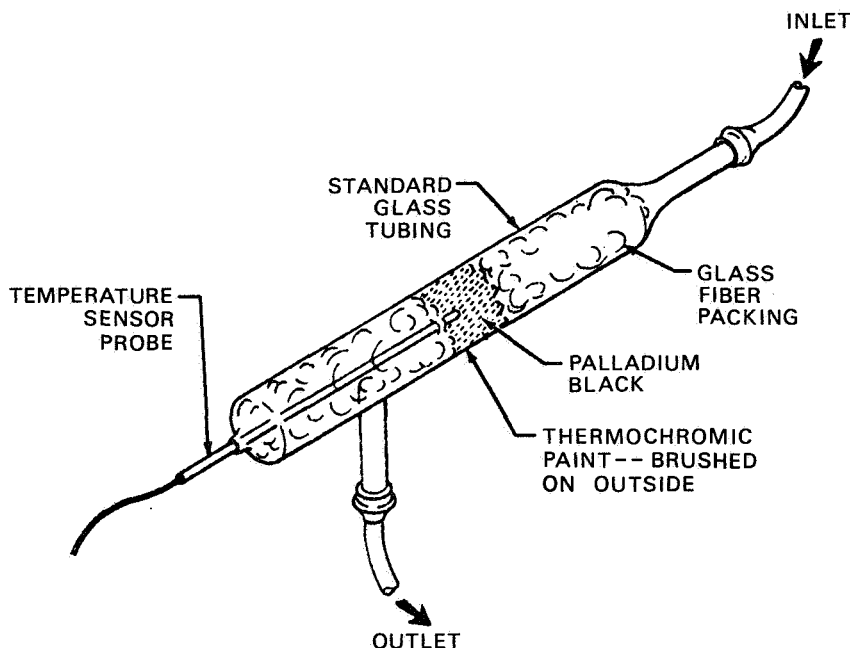


FIGURE 4.—Portable hydrogen detector.

successive color-change points at 55° and 85° C. A temperature-sensing probe is inserted into the mass of palladium black and sealed through one end of the tube to give a continuous, direct indication of thermal changes. The gas to be sampled is drawn through the gas inlet and passes through the palladium black. If H_2 is present, it releases heat when it contacts the palladium black, the amount of heat being directly proportional to the amount of H_2 present. When the temperature of the tube reaches 55° C, the thermochromic paint changes color to give a visual indication of the presence of H_2 . Suitably calibrated, the temperature-sensing probe can be used for direct, quantitative data.

This instrument can be used "as is" for industrial hygiene and air-pollution-monitoring applications as a detector for hazardous concentrations of H_2 . The developers have also used this principle of activated palladium black and thermochromic paint to prepare a continuous, automatic sampling device. In this application a finely woven, but porous, glass-fiber tape is impregnated with the palladium black and coated with a pattern of thermochromic paint. An automatic H_2 detection system could be used in a continuous tape sampler with a color-change monitor.

WELDING GAS MONITORS, WELDING SPECTROMETER ANALYZER

Innovations in welding technology have been among the significant NASA contributions to industrial processing. NASA sets extremely stringent requirements on welds in terms of materials, strength of weld, lack of porosity, minimal weight, and so forth. Heliarc welding is used extensively by NASA for joining aluminum and increasingly more frequently by industry. In the process the weld is made under an inert gas such as helium (He) or argon (A) to avoid oxidation of aluminum. The amounts of H_2 and O_2 in the inert gas affect the quality of the weld, so a monitor was developed to measure these trace constituents. The monitor developed is applicable to air pollution monitoring.

This instrument (refs. 60 and 61) was developed for the Marshall Space Flight Center to monitor the O_2 , H_2 , and A constituents of the inert gas shield used in heliarc welding of aluminum. Even trace amounts of O_2 and/or H_2 in the inert gas can result in an unsatisfactory weld.

This device is a spectrometer that uses photosensitive devices to monitor the emitted light from the inert gas shield (fig. 5). The light is collected through a lens system that incorporates a fiber optics bundle to follow the arc. The light is split in a diffraction grating, and three components (at 6562.8, 7771.9, and 8521.4 Å) go to three photomultipliers (for H_2 , O_2 , and A, respectively). The amounts of H_2 and O_2 are directly read out as ratios to A, which is used as an in-

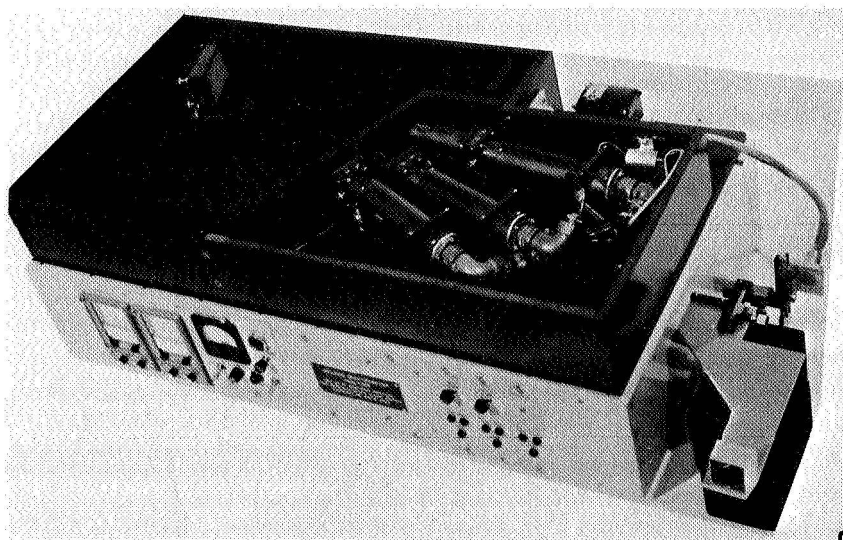


FIGURE 5.—Welding spectrometer analyzer.

ternal standard. The problem of blackbody radiation (background noise) entering the spectrometer is eliminated by the use of an oscillating rectangular prism in the nondispersed light beam. The oscillation causes the emission line to oscillate across the exit slit, which effectively produces an ac signal over the dc blackbody signal.

The instrument is sensitive to less than 5 ppm of O_2 or H_2 in A and is highly reliable. The electronic circuitry is solid state, and circuits have been included that allow use of an oscilloscope for rapid, simple optical alinement of the exit slits.

As constructed, this device detects only H_2 and O_2 , but the design principles can be used to construct a monitor for virtually any gas. A heliarc welding instrument is basically a dc arc, and thus a dc arc could be used as the light source for an air pollution monitor. Photomultipliers responsive to characteristic emission lines of desired gases could then be employed to create an air pollution monitor based on these principles. An automatic continuous monitor is possible, because the gas stream to be measured could be passed continuously through the dc arc, and the output of the photomultipliers could be recorded on a strip-chart recorder or similar readout device. The cost of such an instrument would vary depending on the number of different constituents to be monitored, because each requires a separate photomultiplier and associated electronic circuitry.

CLEAN ASSEMBLY-AREA MONITORING

Contaminants in or on spacecraft and their components have been of great concern for two reasons. First, in a device as complex as a spacecraft, with literally thousands of functioning parts, contamination of even microscopic proportions can result in the failure of a mission, the loss of millions of dollars worth of equipment and effort, and hazards to personnel. An oxide film on a switch, a metallic particle in a valve, or dust motes on an optical surface can hinder the operation of the spacecraft, cause incorrect data to be returned from a sensor, or mean failure of a critical component.

Second, the effect of the experimenter's influence on his experiment is a problem in aerospace research. For example, the detection of the absence or presence of life on Mars will have far-reaching consequences on man's knowledge of the formation of the solar system and, indeed, his total body of knowledge. But if the space vehicle sent to Mars to detect life is already covered, internally and externally, with terrestrial organisms, the experiment will prove a failure.

These considerations have resulted in a great deal of NASA effort in the clean-room field—the use of noncontaminated areas for the manufacture and assembly of spacecraft and their components (refs.

62 through 71). Much work has also been done in sterilization for removal of contaminants. Our prime interest with respect to air pollution monitoring, however, is the NASA-developed technology for measuring contaminants in clean rooms. To determine the efficiency of the various designs and the uses of clean rooms, NASA has sponsored the development of sophisticated devices for measuring small amounts of contaminants. These devices are directly applicable to measurement of pollutants in the atmosphere. They are described in detail below.

Automatic Aerosol Particle Counter

This particle counter, developed by the Royco Instrument Co. and modified by the IIT Research Institute for the NASA Marshall Space Flight Center, monitors particulate contamination in a clean room (refs. 72 and 73). This includes counting the particles, categorizing them in terms of size, and recording the data. For adequate sampling information, counts were necessary at a minimum of three locations within the clean-room area.

The instrument is a light-scattering device; that is, a device in which the number and size of particles present in the sample stream cause a given degree of scattering of a light beam. A transducer head transforms this light signal into electrical signals for data recording.

The particle counter consists of a light source, an optical lens arrangement, and a photomultiplier tube (fig. 6). The filament of the lamp is focused on a slit of known size in a light-shield plate. The lens system images this illuminated slit in the center of a sample stream. A similar lens system and a slit of the same size are used as a receiving system to carry the information to the photomultiplier tube. This arrangement defines an illuminated cube in space. The photomultiplier tube is excited only when a particle passes through this viewing volume. The scattered light intensity is directly proportional to the size of the particle, and thus the signal emitted by the photomultiplier can be calibrated according to particle size. Measurement of the size and number of pulses constitutes the counter. A pumping system conveys the sample stream through the transducer. A concentric air sheath surrounds the sample tube, and filtered air travels through the annular space at the same rate as the sample travels in the inner tube. This arrangement prevents loss of particles into the sample chamber, insuring that particles are counted only once and that the lenses remain clear. The sampling rate is 1 cu ft/min.

This instrument has high reliability and has been used both for tests and as a continuous monitoring device at the Marshall Space Flight Center. It is applicable in its present form for air pollution monitor-

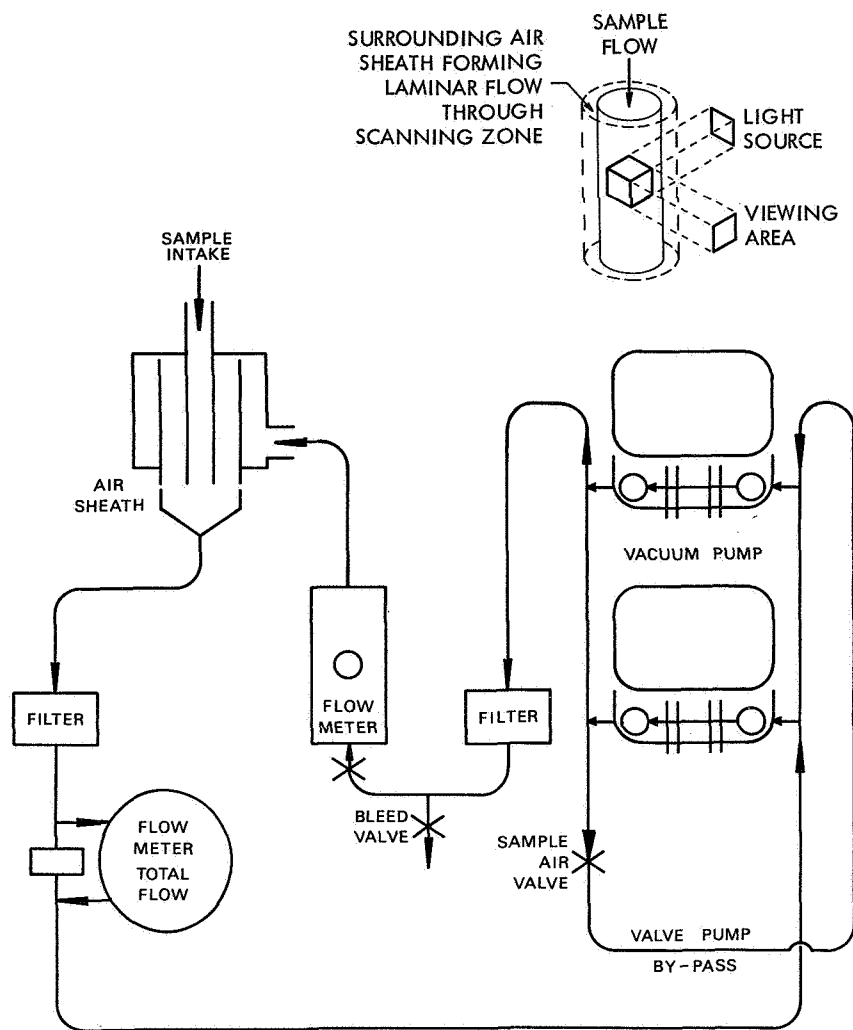


FIGURE 6.—Flow diagram of operation of automatic aerosol particle counter.

ing. Tests by NASA have shown that the count obtained with this instrument is directly proportional to that obtained in visual counting with a microscope—the standard technique. However, this device has distinct advantages over microscopy:

- (1) A microscopist is usually limited to counting particles 5 micrometers or larger in diameter, whereas this instrument can count particles with diameters as low as 0.6 micrometer.
- (2) The instrument requires only minutes per count as opposed to at least 1 hour for microscopy.

(3) The instrument monitors continuously, providing a printed record for analysis of trends and/or association with specific events. It also has an alarm signal when a predetermined limit is exceeded.

The cost of this instrument on a production basis would be approximately \$5000. It can be used by civic and industrial groups concerned with particulate air pollution.

Increased Sampling-Rate Monitor System

This instrument was developed for continuous monitoring of clean rooms (ref. 74). It samples at least 1 cu ft/min of air and counts particles 5 micrometers or larger in diameter.

Standard particle counters, such as the Royco PC200A, have a sampling rate of 0.01 cu ft/min. For extremely clean areas, such as a class 100 clean room (class 100 clean rooms have a maximum of 100 particles/cu ft), this sampling rate is insufficient for adequate measurement.

Sandia Corp. produced this prototype particle counter, which has a sampling rate of 1 cu ft/min. The device uses forward light scattering rather than the 90° scattering used in the Royco-IITRI counter. Adequate particle sizing was not possible because the light uniformity of the optics system was inadequate. However, the particle-count correlation was good.

This is a prototype instrument and no reliability figure has been established. However, the prototype was successfully used for a series of tests for monitoring a clean room, monitoring work locations within a clean room, and checking HEPA (high-efficiency particulate air) filters for leaks.

This device has the same advantages over microscopy that were discussed in regard to the automatic aerosol particle counter, and it is also suitable for civic or research use in air pollution monitoring. It appears to be quite similar to the IITRI-modified device (one of the modifications by IITRI increased the sampling rate of the Royco instrument 140-fold to approximately 1 cu ft/min), with the exception of inadequate particle sizing. This problem can be overcome by modifications to the optical system of the prototype.

Flight-Qualified Aerosol Particle Counter

This instrument was developed by the NASA Electronics Research Center (ERC) in cooperation with Block Engineering, Inc., and the Harvard University School of Public Health to obtain information on aerosol particle buildup in the cabin of an orbiting spacecraft (ref. 75). Because a flight-qualified instrument was needed, weight and power consumption were minimized, and the unit was strengthened and supplied with its own battery power.

The instrument weighs 5½ pounds, its envelope dimensions are 3¾ by 5 by 7½ inches, and its power consumption is less than 4 watts. It operates on the principle of light scattering by single particles and has an air-sampling rate of 1/60 cu ft/min. (fig. 7). The amount of light scattered is a function of the particle size. This is a multichannel instrument, and sorts the information on sizes and counts into one of five channels: 0.5 to 1 micrometer, 1 to 2 micrometers, 2 to 3 micrometers, 3 to 5 micrometers, and 5 to 10 micrometers. This is not a continuous monitor; rather, it is designed for intermittent use for reasons of power consumption. It has built-in sequence timers, and in use it performs the following series of operations after the start button is pushed: a 10-second warmup, a 60-second sampling time, sequential display (via digital Nixie tubes) of the total count in each of the five particle-size ranges, and automatic termination of cycles.

This instrument has been thoroughly tested by ERC and has very high reliability. Battery life is sufficient for about 150 measurement cycles. ERC is currently engaged in refinement of the instrument to lower the minimum particle size measured to 0.3 micrometer (this is possible with an increase in light output), to improve the optical system, and to further miniaturize the electronic circuitry.

This instrument is suitable for use as an air pollution monitor. Its portability, low power consumption, and capability to measure particles simultaneously in five size ranges are not found in commercially available instruments. ERC personnel estimate that the instruments could be produced in volume at a price that would make them acceptable for use by civic and law enforcement groups.

CONTAMINANTS IN FLUIDS

Many fluids are used in spacecraft, and two of these, hydraulic fluid and fuel, must be of exceptionally high purity. Impurities in these fluids are of three forms: dissolved gases, other fluids, and particulate matter.

NASA has sponsored the development of monitoring instruments for dissolved gases and particulate impurities in fluids (refs. 76 and 77). We are including descriptions of these two instruments because they could be useful in air pollution monitoring after pretreatment of the air sample places the impurities in a liquid stream.

Ultrasonic Particle Counter

This instrument (refs. 55, 78, and 79) was designed and fabricated for the NASA Marshall Space Flight Center to detect, count, and size solid particles in a fluid stream. It has been used for monitoring hydraulic fluids, both in continuous and discrete sampling.

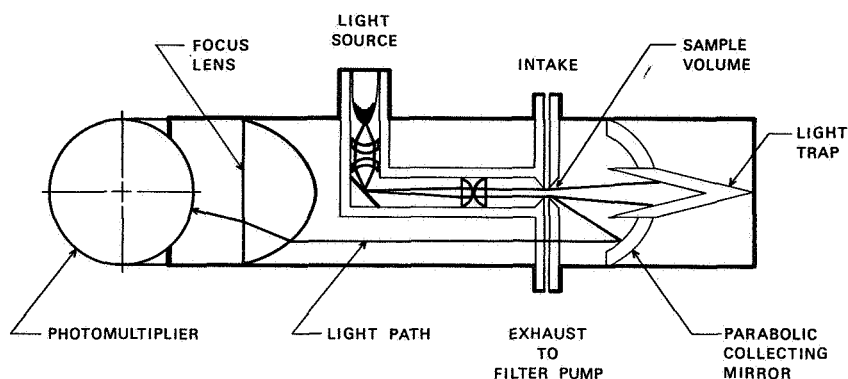


FIGURE 7.—Schematic diagram of flight-qualified aerosol particle counter.

This instrument uses the ultrasonic-reflectoscope method of analyzing echo amplitude from discrete reflectors (particles in the fluid). Two thousand pulses per second of a 5 megahertz frequency signal are passed through the fluid. If the ultrasonic wave hits a particle in the fluid, it is reflected back to the source, and the amplitude of the reflected signal is a function of the particle size. The device detects particles with a diameter of at least 25 micrometers. The maximum flow rate of the fluid is limited by the concentration of impurity and the percentage of the fluid sampled. For essentially 100 percent examination of each unit volume, the maximum flow rate in gallons per minute is made inversely proportional to particle count per volume. Thus, with a concentration of 10 particles/100 milliliters, the flow rate is 500 gal/min; and with a concentration of 100 particles/100 milliliters, the flow rate is 50 gal/min. The particle counting rate is 4000/second.

Skilled technicians are needed to maintain and calibrate the electronic components. Once calibrated, the instrument produces counts that can be correlated with a microscopic count, although the relationship of the correlation is not linear.

This instrument is not suited for use as a remote monitor or mobile monitor for air pollution, but could be used in air pollution research. It would be most useful in counting particles captured in a filter or impactor and subsequently collected in an aqueous solution.

Nonvolatile Residue Nephelometer

This instrument (ref. 55), designed and built by the IIT Research Institute under contract to NASA Marshall Space Flight Center, automatically determines the nonvolatile soluble residue in solvents as a step in the purification of liquid-oxygen systems. Although pure

liquid oxygen (LOX), the most widely used oxidizer in space vehicles, is stable and not subject to deterioration, mixtures of LOX with most organic materials explode under impact. Even the grease from fingerprints left on aluminum valves and transport lines during assembly has combined with LOX, and the mixture has caused explosions.

Thus, exceptional measures are taken to insure removal of incompatible organic materials and traces of grease from all LOX systems. After cleaning and degreasing, the systems are inspected by rinsing them with highly purified trichloroethylene or Freon, and the rinsings are examined for traces of contamination to verify the thoroughness of the cleaning. In the standard laboratory method, the traces are extracted by evaporating the rinsings just to dryness and then weighing the residue to determine the nonvolatile, soluble residue (NVR). The nephelometer is an automatic device for determining the presence of NVR in the solvent without going through this long, tedious procedure.

The instrument is based on the light-scattering characteristics of an aerosol spray of the solvent. Solvent is continuously fed to a nebulizer, in which it is atomized with a large volume of air to produce micrometer-size liquid particles of solvent and soluble contaminant. The large volume of air evaporates the volatile solvent, and the NVR is left behind as an aerosol in trichloroethylene vapor and air. The aerosol particle size depends on contaminant level. The aerosol, surrounded by a clean air sheath, is fed to a photometer, and the scattered light from a defined field of view is measured. The amount of scattered light is a measure of the contaminant level. The NVR nephelometer has two modes of operation; one in which a signal is given from a single sample, and one in which the contaminated sample is compared to a reference sample.

The device is quite reliable. Tests at Marshall Space Flight Center have shown that once calibrated, the instrument provides accurate analysis of the NVR in chlorinated solvents within 40 seconds per sample. These tests have been compared with the standard laboratory procedure, and a high degree of correlation has been found. The device will detect down to 0.1 to 0.5 milligram of degreasing NVR/1 solvent.

This device is useful in air pollution research for determining products of industrial processes, and for checking solvent purity and decreasing efficiency in general industrial application. It is not a general air-pollution-monitoring device but could be useful in research or industry where there is a requirement to measure NVR that might be released into the atmosphere. For such an application, it is much faster and as reliable as the standard laboratory method.

BIOSPHERE STUDIES

The interest of NASA in microbiological content of the Earth's atmosphere is threefold. First, NASA research vehicles (spacecraft) permit men to measure biological life at high altitudes for the first time. Second, techniques for detecting life on other planets are being tested in the Earth's atmosphere. Third, as mentioned in the section "Clean Assembly-Area Monitoring," spacecraft sent to other worlds must not carry terrestrial organisms with them. Thus, NASA must know to what extent a spacecraft can become biologically contaminated as it passes through the atmosphere.

These studies (refs. 80 through 90) and the techniques and instrumentation developed in their course are important to air pollution monitoring. Most obvious, of course, are the collection techniques that have been developed. Several of these are applicable to collection of any type of particulate matter from the atmosphere. Also of interest are sampling and counting techniques, because microbiological contamination is a form of air pollution (i.e., in hospitals), and also because air pollution research makes use of vegetative and spore cultures for particles in aerosols.

Accordingly, some of these NASA developments that are novel and/or improved instruments or techniques applicable to air pollution monitoring will be described below.

Air Sampler for Minute Particles

This instrument (ref. 91) was designed and fabricated for collection of extraterrestrial dust greater than 0.1 micrometer in diameter. The particles were to be both collected and protected for use in analysis.

The device consists of an air-ejector impactor sampler that causes impaction of particle-laden air onto several collection surfaces within a collection cylinder (fig. 8). When not in operation, the collection cylinder is retracted within a protective envelope.

An air-ejector pump, comprised of a compressed gas source and associated tubing, valve, and flowmeter, simultaneously sends compressed gas through valves to a nozzle in a diffuser and into a pneumatic actuator. The gas flow into the actuator extends the collector from the retracted position to the exposed position. Gas flow into the nozzle and diffuser entrains surrounding air and produces a reduced pressure within the collection cylinder, causing air to flow through its impactor slits and particles to impact on the collection surfaces within. When the gas flow is shut off, a spring draws the collection cylinder back into the protected position.

This device has been shown to have high reliability because it uses a compressed gas for power (the only electrical power required is for

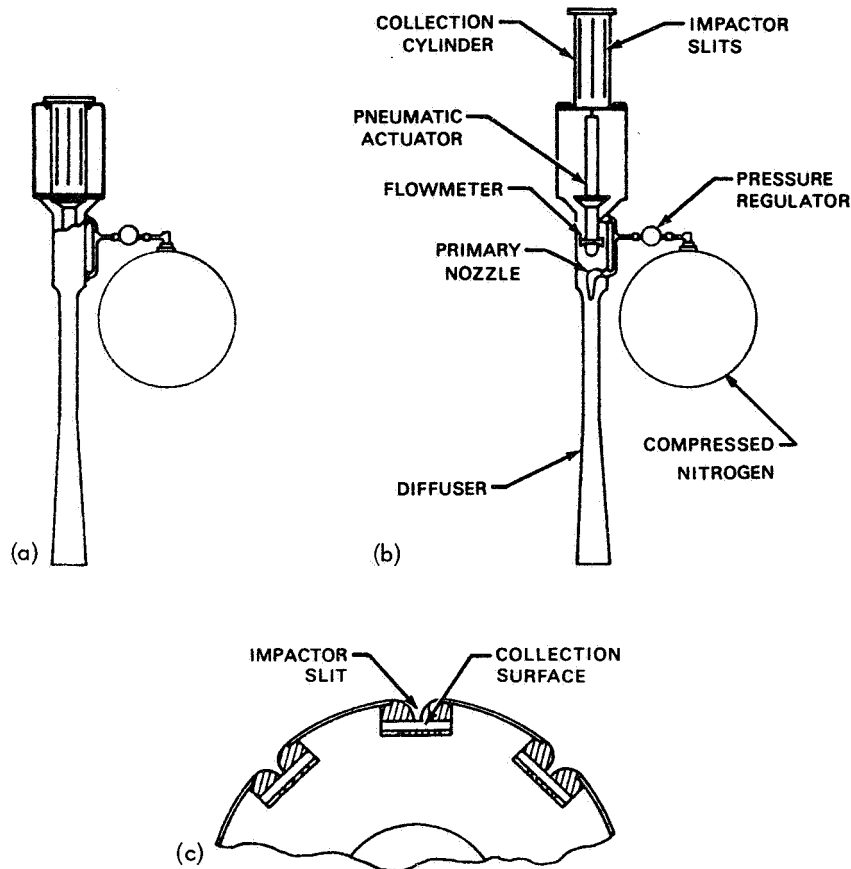


FIGURE 8.—Air sampler for minute particles.

the valve, and that can be provided by batteries) and is very simple to operate.

This is an excellent device for airborne collection of particulate matter at any altitude. Its primary application would be for aircraft monitoring. However, the device can operate in a stationary position, because it produces its own airflow.

Several instruments for sampling biological species at high altitudes have been developed by NASA efforts. These are relatively sophisticated units using motor-driven, air-movement devices for sampling at high altitude and eliminating microbiological contamination while reaching sampling altitude. For these reasons, these devices appear to be overly complex for the requirements of air pollution monitoring. Nevertheless, the Litton Mark II and Mark III sampling systems (ref.

92), the NCAR Corp. enclosed cryocondenser for air recovery (ref. 93), the University of California microbe sampler (ref. 94), the NASA Jet Propulsion Laboratory work conducted by Gerald A. Soffen (ref. 95), and the X-15 mounted micrometeorite collector may be of interest to air pollution researchers.

Wolf Trap Mars Microbe Detector

This instrument (ref. 96) was designed and built by the University of Rochester for NASA. It was designed to detect microbial life on the surface of Mars and has features necessary for surviving launch and Martian environments.

The device collects soil samples and places them in five separate enrichment cultures. It then optically monitors the cultures for evidences of turgidity caused by multiplication of microbiological organisms. A sensitive pH monitor measures the acidity changes in each culture. The device has been tested in the Mojave Desert and successfully detected life. Engineering for space-flight requirements insures a very rugged device. Standard laboratory culturing and counting techniques are usually less expensive and more reliable. However, in cases where remote monitoring might be necessary, this device would be applicable.

A device operating on the principle of microcalorimetry, that is, detection of a very small amount of heat, has been produced by Beckman Instruments for NASA Ames Research Center.

Another instrument for remote detection of life employs the "firefly reaction," that is, the generation of light that occurs when the firefly enzyme, luciferin, reacts with adenosinetriphosphate (ATP). An instrument to extract ATP from a soil sample, introduce luciferin, and monitor the light produced (if any) has been produced by Hazleton Laboratories for the NASA Goddard Space Flight Center (refs. 97 through 103).

These instruments were designed for life detection on Mars and, though operating on different principles, have the same utility for air pollution monitoring as the Wolf trap.

NASA Air Pollution Studies

AIR POLLUTION MONITORS

Measurements of air pollution from satellites is a possibility, and NASA has sponsored research in this direction. Although such remote sensing cannot replace surface (and near-surface) monitoring, it can be used for global distribution, buildup, and dispersal measurements as functions of meteorological conditions. Such measurements can be made with such instruments as lasers, infrared sensors, and microwave equipment. Much information is necessary to determine the characteristic emission bands of pollutants that could be detected by such satellite-borne instrumentation. Further, the signal-to-noise ratios of the instrumentation must be established to give indications of what types of measurements are possible, how sensitive they can be under optimum instrumentation development, and what types of instrumentation hold the greatest profit.

To these ends, the NASA Electronic Research Center in Cambridge, Mass., has funded a "Study of Air Pollution by Remote Methods" (refs. 104 and 105). The study has been underway only a short time, and no instrumentation for use for air pollution monitoring has been developed. However, pollutant characteristics have been established and work has been started on evaluation of various remote sensors such as the radiometer, dispersive spectrometer, interferometer, microwave radiometer, and laser systems and a long-path infrared radiometer. This work will result in much useful information in air pollution monitoring.

Two instruments designed by NASA for use in air pollution monitoring are covered below.

Ultraviolet Densitometer

This instrument (refs. 106 and 107) is being developed at the NASA Flight Research Center with the cooperation of Plasmadyne Corp. and with Beckman Instruments, Inc. The objective is a technique for remotely measuring free-stream air densities at high altitudes. Because of interferences from Mie scattering, the device is also capable of detecting particles in the atmosphere.

An optical transmitter projects a beam of ultraviolet light away from its source. A receiver near the source views an area of the trans-

mitted beam. The resulting intersection volume contains the gas whose density is being measured by light scattered back to the receiver by the intersection volume. The receiver collects light that is scattered either from air molecules or from particles in the atmosphere (fig. 9).

The device is in the developmental stage, and details concerning operating distance, molecular concentration, composition, and so forth, are not available. The present reliability is also very low, because the light source is a pulsed arc that has a tendency to shift both in wavelength and intensity. Electrode disintegration occurs at an unacceptable rate because of high-temperature operation. In addition, the pulse source creates large transients in the receiver electronics.

The cost will be quite high if the ultraviolet arc is used as the illumination source. There are no commercially available instruments similar to this device. As it stands, this instrument is not suitable for conversion to air-pollution-monitoring instrumentation. The basic concept is of interest for determining gas composition and temperatures, but interferences from Mie scattering in the atmosphere may invalidate information from this device for low-level operation.

Infrared Tunable Laser

This instrument (refs. 108 and 109) is under development at the NASA Electronics Research Center as an air-pollution-measuring device.

The laser system operates similarly to the ultraviolet densitometer discussed above. A beam of light from an iodine infrared laser or from a CO_2 infrared laser is passed through the atmosphere to a reflector and back to a detector. The laser is tunable; that is, the laser can be forced (by placing in front of the laser source a given concentration

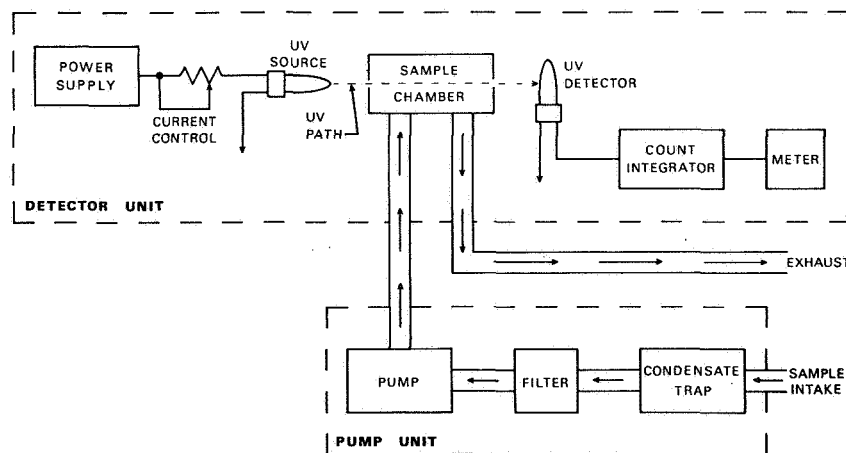


FIGURE 9.—Flow diagram of operation of ultraviolet densitometer.

of a gas such as propylene) to emit specific spectral lines that fall on the characteristic infrared absorption bands of certain air pollutants. Thus, the amount of attenuation of the light laser of a specific spectral line is a measure of the amount of a given air pollutant. The narrow spectral width of the laser emission permits sensitive detection, minimizes interference among various pollutants, and allows penetration of the atmospheric water-absorption bands. The collimation and high-power outputs available from lasers permit transmission of the radiation over long straight paths through the atmosphere and over long folded paths in multiple-pass absorption cells.

With a $\frac{1}{2}$ -kilometer path to a retroreflector and back, it is predicted that the following pollutants can be detected:

Pollutant	Concentration, ppm	Laser line used
Carbon monoxide.....	2	4.86 μm I_2
Nitric oxide.....	1	5.5 μm I_2
Ethylene.....	0.1	10.53 μm CO_2
Sulfur dioxide.....	1.5	9.08 μm CO_2
Ozone.....	0.15	9.52 μm CO_2

It seems feasible to extend the technique to other gases. Because this is a developmental device, no cost or reliability factors are available. Effort is being expended on constructing the transmitting and receiving equipment and making the laser portable. A prototype instrument is now under construction.

There is no immediate applicability of this instrument to air pollution, but the theory and the practical work done thus far indicate that a novel and very useful technique is being developed by NASA. Tulane University will use the prototype laser for tests.

FUEL CELLS FOR POWER GENERATION

Many air-pollution-monitoring instruments must be placed in relatively inaccessible locations or be used in mobile monitoring without access to commercial power supplies. There are currently no weight or size requirements for this instrumentation as stringent as those encountered in space travel. Conventional power sources, such as batteries, are usually adequate, but the development of fuel cells offers an opportunity for improvements in power generation for remote or mobile air pollution instrumentation (refs. 110 and 111).

A fuel cell is an electrochemical device in which most of the free energy of reaction of one or more chemical species can be directly

transformed into electrical energy. Reactants are added on demand, and products are removed as required. Fuel cells are classified as primary or secondary. In the former, reactants are used only once; in the latter, reactants are regenerated for reuse. Because they are devices for direct conversion of chemical to electrical energy, fuel cells are not limited by the Carnot-cycle efficiency limitations, and thus have a theoretical efficiency of 80 percent. Fuel cells with efficiencies as high as 65 percent have been produced, whereas heat-cycle engines have reached only 40 percent. Because there has been no mass production of fuel cells, their cost is still relatively high. Also, power densities are still too high. Costs will be reduced as more applications for fuel cells are realized. One possible application of fuel cells is in mobile and remote monitoring of air pollution.

Glossary

aliquot: a part of a number that divides the number without a remainder.

biosphere: the sphere of living organisms, which penetrates the lithosphere (land), hydrosphere (water), and atmosphere (air).

colorimetric: pertaining to measurement by hues and/or intensity of color.

conductometric: pertaining to measurement by heat or electricity transmission capability.

corona: discharge of electricity that appears on the surface of a conductor under high voltage.

ecologic: describing biology as it deals with the mutual relations between organisms and their environment.

exothermic: formed with evolution of heat.

gravimetric: pertaining to measurement by weight.

interferometer: instrument using light interference phenomena for measurement of wavelengths.

nebulizer: device for reducing to a fine spray, an atomizer.

offgas: to vaporize or sublimate.

planimetry: measurement of plane figures.

pyrolyze: heat or burn, not necessarily in oxygen-containing environment.

radiometer: instrument measuring intensity of radiant energy by the torsional twist of a suspended disk blackened on one side.

thermochromic: pertaining to measurement by color change caused by heat.

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