Development of Solid State Samplers for Work Atmospheres

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National Bureau of Standards
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ABSTRACT

A program is described for evaluating the efficiency of solid sorbers for collecting trace quantities of hydrogen fluoride, phosphine, hydrogen cyanide, chlorine, and fluorine in work atmospheres for subsequent laboratory analysis. The gas handling and sampling instrumentation is described, and experimental results to date are presented.

Sodium acetate is a very efficient sorber for hydrogen fluoride, and its solubility in water proves to be highly advantageous for subsequent HF determination by ion selective electrode. Potassium permanganate impregnated silica gel sorbs phosphine effectively, and Ascarite has been found to sorb hydrogen cyanide, but quantitative experiments on the latter two systems are still in progress.

Work on chlorine and fluorine systems will be initiated in the near future.

1. INTRODUCTION

The report summarizes work on the development of sampling procedures and devices for the collection of five toxic gases in industrial atmospheres, viz. fluorine, hydrogen fluoride, hydrogen cyanide, chlorine, and phosphine during the period January 1 - June 30, 1974. The program is being carried out under a Memorandum of Agreement between the National Bureau of Standards and the National Institute for Occupational Safety and Health.

The scope of the work includes investigation of various sorbent materials and selection of appropriate sorbents based on criteria of stability, cost, and effectiveness; and development of suitable collection devices and analytical methods for determining the contaminant levels collected.

To date, the experimental techniques have been developed for sampling and analyzing the contaminant gases. Data have been obtained on the sorption of hydrogen fluoride, phosphine, and hydrogen cyanide on various solids and prototype sampling tubes for hydrogen fluoride have been prepared and tested.

2. DEVELOPMENT OF METHODOLOGY

The project has been divided into several discreet categories, each of which is discussed in detail in the sections that follow. In this section the technical parameters of the

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problem are analyzed, various solutions to the problem are considered, and finally decisions are made on at least one approach that can be used for each area of concern. The block diagram of Figure 1 illustrates the general approach that was followed:

(a) By using a single analytical procedure for each contaminant, the results from the solid-state sorbent experiments may be easily compared to the results obtained with standard wet collection procedures.

(b) Reliable flow controls for both the solid state and the wet sampling assure that known amounts of contaminant gases are trapped.

(c) The use of a compressed gas cylinder as a contaminant source provides a sufficient quantity for a large number of tests and experiments.

The procedures and considerations applied to this project are general in nature and should be applicable to the development of solid-state sorbents for a wide range of contaminants.

2.1 Contaminant Generation Systems

To carry out the many tests required for the screening and selection of solid-state sorbents, a reliable contaminant source is required. The gases needed are all obtainable commercially as the pure gases in compressed gas cylinders. For this work, however, concentrations are required which in some instances are less than one-millionth of the pure gas, far too low a concentration to be reliably obtained by diluting the pure gases in a dynamic flow system. However, four of the gases are available commercially in the concentration ranges needed, and these were obtained from the producer. The gases and nominal concentrations are listed below:

HF	50 ppm
HCN	50 ppm
Cl_2	5 ppm
PH_3	4.5 ppm
F_2	1% or 10^4 ppm

The lowest fluorine concentration available is one percent and this will require further dilution to achieve a level low enough for this investigation.

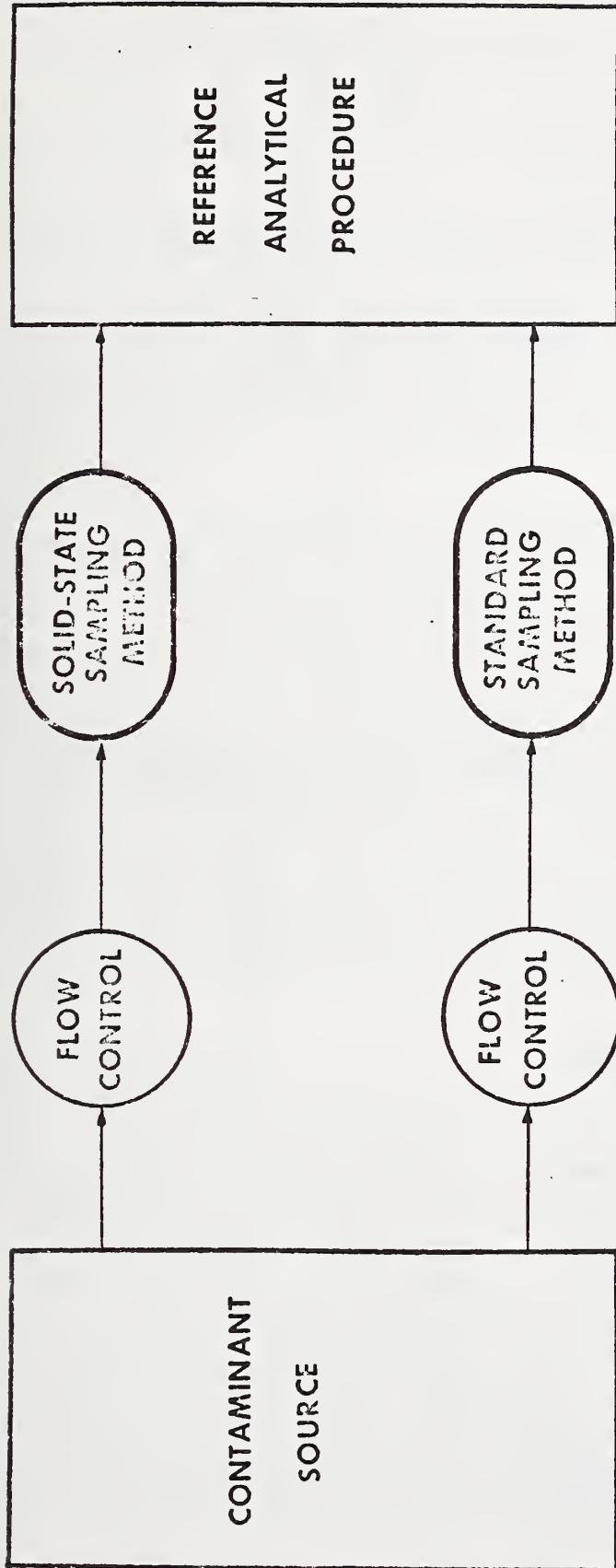The above concentrations were chosen for the following reasons:

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Figure 1. Block Diagram of Program Organization

(a) The nominal concentrations equal or exceed the highest levels required for this project.

(b) The gases can be used undiluted for rapid screening of candidate sorption tubes.

(c) The entire range of needed concentrations can be obtained simply by using a suitable gas dilution system.

The cylinders were supplied with nitrogen as the diluent gas. For screening of tubes, the fact that nitrogen was the background gas rather than air did not cause any observable problems; for analysis at the lower concentration levels breathing air or in-house compressed air was mixed with the contaminant gas.

To obtain gas concentrations ranging from 1/5 to 5 times the TLV (Threshold Limit Value), a gas dilution system as illustrated in Figure 2 is required; several systems of this type have been constructed and used successfully in earlier projects involving dilution of gas mixtures [51]. The mixing system illustrated uses air to dilute the contaminant gas so that the composition of the matrix gas is effectively air rather than nitrogen, especially at the lowest concentration levels. This dilution system can also be used to study the effect of humidity on the sampling efficiency of solid sorbents. By inserting a water saturator into the diluent air stream, water-saturated diluent air can be delivered to the mixing manifold. At a ratio of diluent air to contaminant of 24:1, a final mixture of 1/5 TLV can be achieved having 96 percent relative humidity. Other relative humidities are obtained by varying the flow rates of the gas streams.

2.2 Gas Sampling System

In devising a gas sampling system, certain requirements were necessary: flow rates as low as 50 ml/min and as high as 1 liter/min were needed; constant flow at each of the flow rates was required so that errors resulting from flow, and hence volume, measurement could be kept to an absolute minimum. Ordinarily, vacuum sampling using a critical orifice is the preferred method. In this case, however, three critical orifices would have been needed for the flow rates at 50 ml/min, 200 ml/min and 1 liter/min. Furthermore, a critical orifice maintains constant flow only when the upstream pressure drop is kept constant within a narrow range, and since the experimental design required that one or more solid-state sorbents and bubblers would be needed, the pressure drops would thus change and periodic recalibration of system flow rates would have been required.
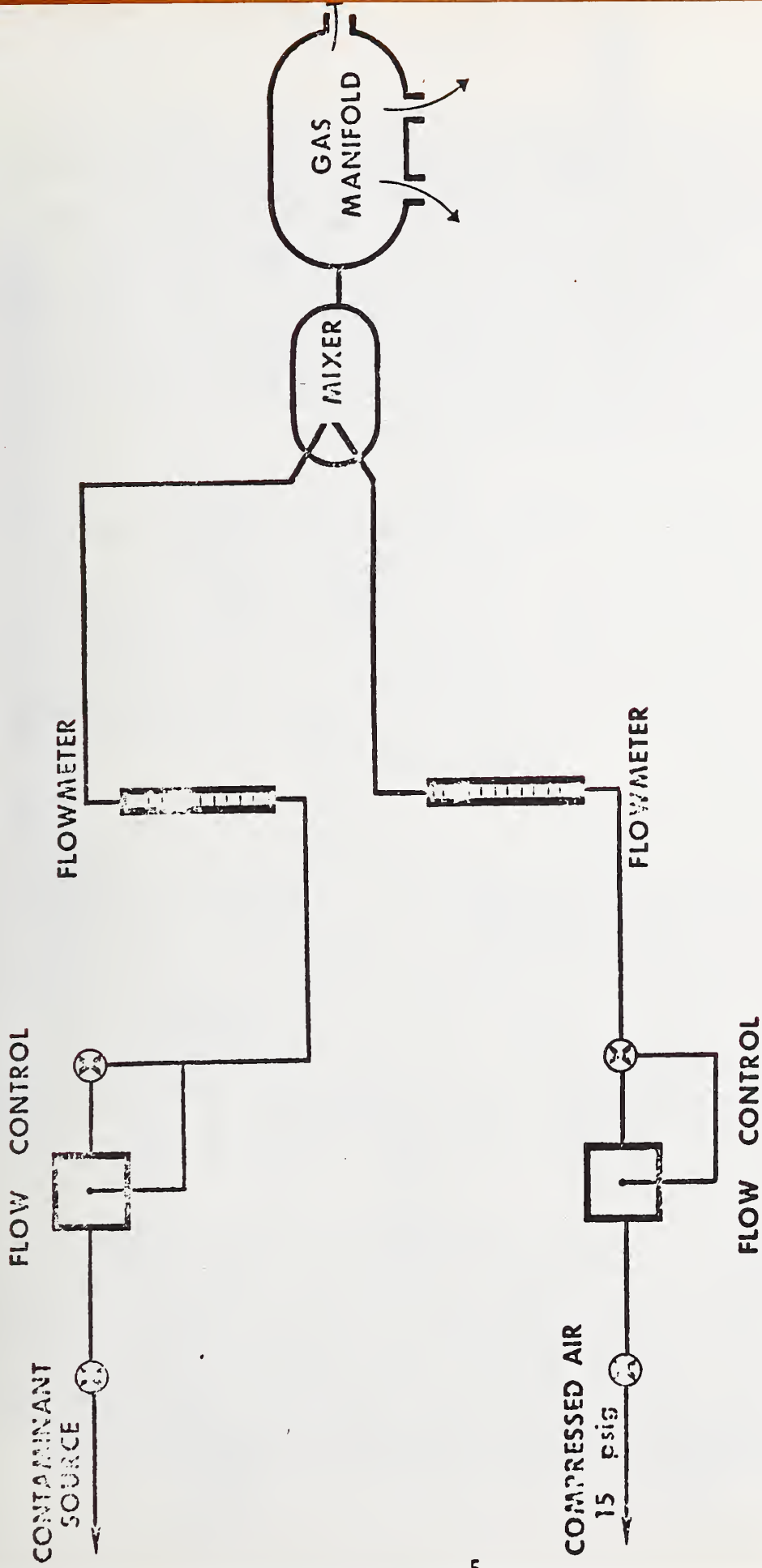
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GAS MANIFOLD

MIXER

FLOWMETER

FLOWMETER

FLOW CONTROL

FLOW CONTROL

CONTAMINANT SOURCE

COMPRESSED AIR 15 psig

Figure 2. Diagram of Gas Dilution System

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To avoid these problems, a new sampling system, shown in Figure 3, was designed. The system contains a downstream flow controller and needle valve and is connected to a constant-vacuum source (in this case an air sampling pump). The vacuum is kept constant at about 100 mm Hg and the needle valve can be adjusted so that any flow rate between 50 ml/min and 1 liter/min can be selected. It has been found that pressure drops up to approximately 400 mm Hg* are tolerable and the flow will remain the same at a pressure drop of 400 mm Hg as at zero mm Hg. This means that as many as 10 sampling tubes and bubblers may be inserted in the system without changing the flow rate.

This system maintains a preset flow to within ±2 percent for sampling periods ranging from minutes to hours. Flow rate is easily set by using the 3-way valve (Figure 3) to switch to a calibrated rotameter and adjusting the needle valve to the desired flow rate. The sampling of the contaminant gas is performed by loosely inserting a sampling tube or impinger into the sampling manifold. The sampling manifold receives the contaminant gas from the gas dilution system where the flow rate is adjusted so that it is at least 1.5 times the sampling rate, thus assuring that no ambient air is drawn in by the sampling system.

2.3 Solid-State Sorbents

Solid-state sorbents have been in wide use for many years in the detection of industrial contaminants and air pollution. For the most part they have served to qualitatively or semi-quantitatively identify a contaminant or class of contaminants and have most frequently been in the form of the familiar detector tubes and the reagent-impregnated filter paper. More recently solid sorbents have been used for quantitative determinations of gaseous fluorides; in this case, they have been either in the form of a coated tube [52] or a treated filter paper [53]. Of course, the most successful application of solid-state sorbents to date has been in the quantitative determination of organic vapors by adsorption on charcoal tubes [57].

Capture of a volatile contaminant can be achieved by the mechanisms of adsorption or reaction. Three general routes are recognized. The first is the adsorption route in which the solid-state sorbent captures the unchanged contaminant which can then be analyzed either directly or by chemical conversion to a species which is then analyzed. The second and third routes represent capture by chemical reaction, and the product of this reaction can either be the final reaction product for which an analytical method is available or an

*400 mm Hg = 3.00 Pa; 1 Pa = 1.333 x 10^2 mm Hg
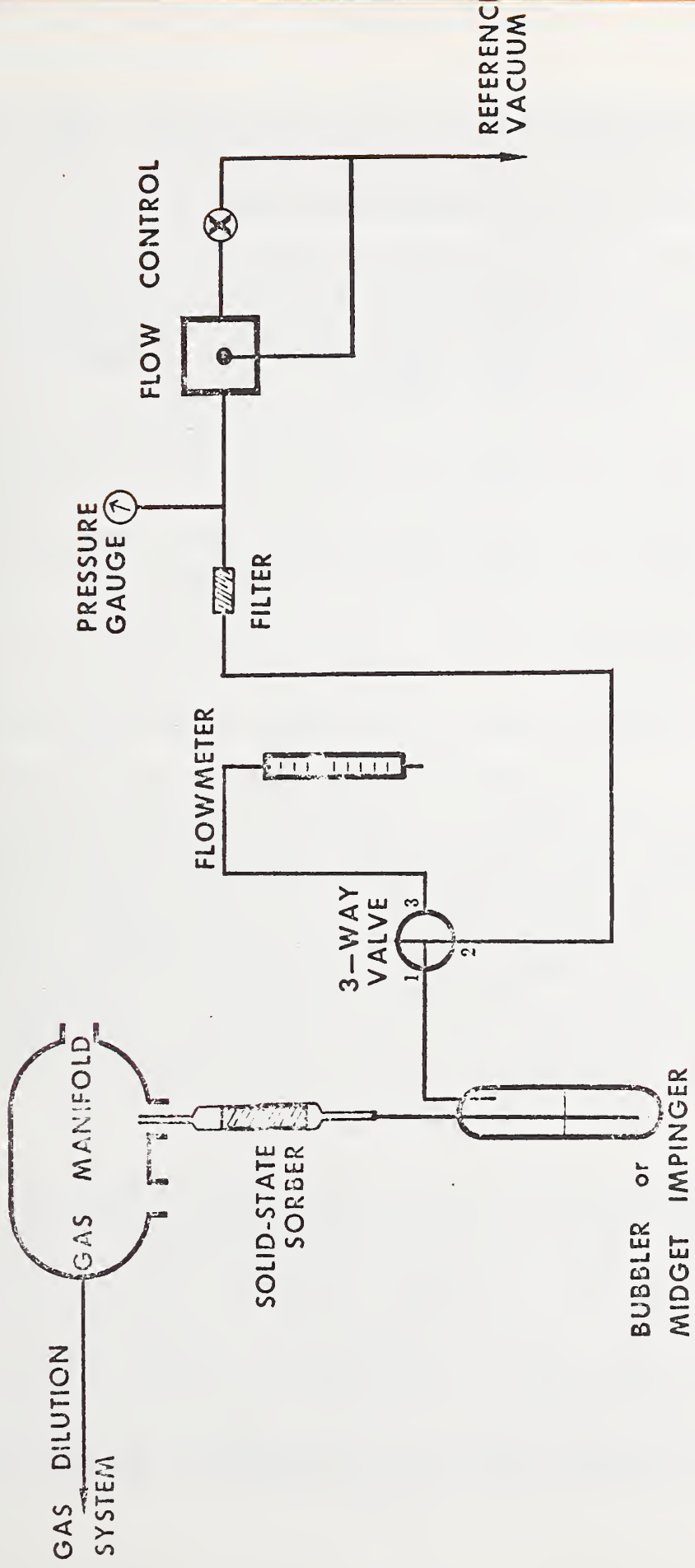
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Figure 3. Diagram of Gas Sampling System

intermediate product which can be converted to the final
reaction product.

2.3.1. Solid-State Sorbent Requirements

In addition to some obvious requirements that a sorbent
device must possess, namely sufficient capacity to quantita-
tively capture a contaminant and, during the analysis phase,
to quantitatively desorb the contaminant, many other charac-
teristics are required. Several are listed below and various
technical solutions are offered:

1. The resistance to air flow should not be greater
    than 25.4 mm Hg at a flow rate of 1 liter/min
    (as specified by NIOSH).

2. The device should be stable to the effects of
    humidity, temperature and storage.

3. The device should indicate if breakthrough has
    occurred.

4. The device should retain the contaminant of interest
    in the presence of other substances in the air.

The air flow requirement can be met by a suitable choice
of sorbent tube geometry. An adsorbing medium such as char-
coal or silica gel of, say, 20/40 mesh size could be used
in a sampling tube, which would then have flow characteristics
similar to the charcoal tubes now used for organic vapors.
Similarly, for tubes containing a reactive material, the mesh
size of this reactive material could be suitably chosen; or
alternately the reactive material could be coated onto selected
substrates such as glass beads, charcoal, or silica gel of
the proper mesh size. Devices other than packed tubes can
be fabricated to meet the flow requirement. For example, a
treated filter paper or a tube packed loosely with treated
glass wool could also be designed to meet the flow require-
ment.

The effects of humidity, temperature and storage on
the tube containing the contaminant cannot easily be
predicted. In the case of HF and HCN, capture of the
acidic gases can be accomplished by reaction with basic
reagents, and the resulting fluoride and cyanide ions should
be stable. For F_2, Cl_2 and PH_3 stability will have to
be determined. (Further discussion of proposed ways of
capturing these gases is presented in the Gas Analysis
Section).

A visual indication of breakthrough of the contaminant
gas can be achieved by placing downstream from the sampling

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tube, either in a separate tube or as a back-up section, a color-change reagent which would signal breakthrough. Alternately, a back-up section, isolated from the analysis section of the tube by a separator, will permit indication of breakthrough by laboratory analysis.

Finally, the requirement that the device retain the contaminant of interest in the presence of other substances, would appear to be easily met for the cases of HF and HCN, since these gases are converted to the non-volatile anions. Similarly, if the final choice of device for F_2, Cl_2 and PH_3 employs a reaction to produce a non-volatile species, then this requirement could also be met for these contaminants.

Another practical requirement should be noted. As will be shown in the Gas Analysis Section (2.4) most procedures for capturing contaminant gases by chemical reaction involve reactions in water. Hence, it may be necessary for the trapping medium to contain enough water for reaction to occur. If the humidity of the sampled air is high then this may be sufficient; however, sampling in atmospheres of low humidity may present problems. The use of a humectant, such as glycerin, in the preparation of the sampling media has been proposed as a solution to this problem [54].

2.3.2. Literature Survey of Solid Sorbents

Classical methods of trapping contaminant gases from the atmosphere for subsequent chemical analysis recommend liquid sorbers having nearly 100 percent efficiency. Solid sorbers have been mentioned in the literature for trapping atmospheric gases (e.g. sodium carbonate for sorbing HF), but most often they have been mentioned for specific applications such as color indicators for Draeger type tubes, or cigarette filters for removing specific materials (such as solid particles or HCN) from cigarette smoke. This section describes some solid and liquid sorbers which have been mentioned in the literature.

A. Fluorine and Hydrogen Fluoride Sorption

Most collections of fluorine and hydrogen fluoride have been carried out in bubblers or midget impingers using water or aqueous alkali solutions such as 0.1 N NaOH to trap the acid gases. Solid sorbers impregnated with alkali have been reported in recent citations; these have been of direct interest.

ASTM D 3269-73T mentions filter papers impregnated with calcium-based fixative agents such as low-fluoride calcium oxide or other soluble alkalies, and cautions that gaseous fluorides collected on glass fiber filters cannot be quantitatively removed by leaching with water. Alkali impregnated

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filter paper is mentioned also by Marshall and Wood [16], and by Huygen [17] who have compared the efficiency of (a) Whatman No. 1 paper impregnated with 20 percent KOH-10 percent glycerol and (b) paper impregnated with 20 percent KOH-10 percent triethanolamine, with bubblers containing 0.1 N NaOH. Huygen found essentially 100 percent collection efficiency for freshly prepared filters at humidities greater than 25 percent; at 0 percent humidity the efficiency was 87 percent. Hermann [10] used silver balls coated with a thin layer of sodium carbonate in a quartz tube, comparing this sorber with alkali-treated paper tape and sodium bicarbonate coated tubes. Guilbault [19] has described paper tape impregnated with Mg-8-hydroxyquinoline to give ppb detection capability by quenching of fluorescence. Okita (1972) [23,24] has collected gaseous hydrogen fluoride on filter papers impregnated with 1 percent sodium carbonate and potassium carbonate using a permeation tube to generate HF. Analysis using Alizarin complexone spectrophotometry or specific ion selective electrodes at concentrations of 0.05-1.0 ppm showed the filters to have 94 percent collection efficiency at 40 percent relative humidity.

Desbaumes [18] et al. have used a fluidized bed of silica gel impregnated with 3 percent triethanolamine, eluting the adsorbed gases with hot water. Salyamon and Popelkovskaya (1973) [25] sorbed HF on silica gel for subsequent determination of fluoride ions in air and water by twenty-five different photocolorimetric methods. (They found that the criteria of specificity, accuracy, and reproducibility were satisfied best by the methods using reagents Zr-Eriochrome Cyanine; Zr complex of 4-sulfophenylazo-1,8-dioxynaphthalene-3,6-disulfonic acid; and Ce-Alizarin complexone.) Tsujimura et al. (1971) [26] recovered about 90 percent of fluorine from a mixture of fluorine, nitrogen, and oxygen on columns of silica gel and activated alumina.

Some miscellaneous solid sorbers are membrane filters impregnated with sodium formate [13]; and polystyrene filters impregnated with 10 percent sodium formate in 50 percent ethanol, the latter being dissolved in buffered ethyl acetate for direct determination of HF by an ion selective electrode [12].

B. Chlorine Sorption

As with fluorine and hydrogen fluoride, chlorine has been collected in liquids such as water or 0.0125 N NaOH solutions; or in acidified potassium iodide or methyl orange solutions for direct colorimetric measurement. Elinson et al (1973) [34] have described a chlorine-specific solid sorber consisting of potassium boride and sodium carbonate soaked silica gel containing fluorescein indicator. The sorbent was chlorine-specific except for partial CO_2 sorption.

A brief reference to the efficiency of activated charcoal for retaining chlorine is given in ASTM D 1605-60. At 20°C and 760 mm Hg, the maximum of chlorine that the carbon retains when flushed with uncontaminated air is 15 percent. This represents the practical sorption capacity for atmospheric collection. For comparison, the retention is 8 percent for HF, zero for water.

C. Hydrogen Cyanide Sorption

Classical methods of HCN sorption use bubblers or impingers filled with water or aqueous alkali. Since cyanide can be lost by volatilization, stabilization at a pH above 12 is important (ASTM D 2036-72). Solid state sorbers mentioned in the literature include filter paper impregnated with ferrous sulfate and alkali (giving Prussian blue as a color detection when subsequently submerged in dilute sulfuric acid) [14,41] and silica gel impregnated with silver chloride, mercurous chloride, or other metal salt to yield insoluble cyanide and free HCl (the latter being detected with an indicator such as bromothymol blue or bromcresol green) according to a German patent mentioned by Bark and Higson [37] Mercurous diphenylcarbazide paper wetted with 3 percent NaHCO$_3$ has been used by Tanaka and Yamamoto (1961) [42] who found a linear relation between the length of the pink zone and the amount of HCN, up to 6 µg/100 ml air.

Solid sorbents for HCN have been investigated by cigarette filter manufacturers, because HCN is produced in tobacco smoke. Filters of paper or cellulose acetate are used plain or impregnated with, e.g. polyethyleneimine and/or zinc acetate plus a humidifying section of encapsulated water [43] to give about 83 percent trapping efficiency; or with zinc oxide and triacetin, tri-or tetra-ethylene glycol, triethyl citrate or similar substance [44] to give a trapping efficiency of 50-60 percent, passing 80 µg of HCN as compared with 210 µg for untipped cigarettes.

D. Phosphine Sorption

Liquid and solid sorbers have been described for the direct reaction of phosphine with color-forming reagents. Dechant et al. [47] have collected phosphine in a pyridine solution of Ag-diethyldithiocarbamate and read the color of the stable complex down to 0.05 ppm. The collection efficiency of the sorber is 86 percent. Solid sorbers for phosphine include impregnated papers and silica gel. Hughes and Jones (1963) [48] describe silver nitrate impregnated filter paper; the visible spot can be compared with standard stains or else removed with hot HNO$_3$ and reacted with sodium sulfide and boric acid for spectrophotometric determination at 470 nm.

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Silica gel impregnated with AuCl₃ is described by Kobayashi and Meguro (1967) [49] as a detector tube where 0.03-150 ppm phosphine can be determined by the length of the colored zone. Muthu et al. (1973) [50]describe mercuric chloride papers with methyl yellow indicator which turn from yellow to red upon the liberation of HCl [by formation of $P(HgCl)_3$]. Nelson and Milun (1957)[56]have determined phosphine in air at ppb levels by metering known volumes of air through tubes packed with silica gel impregnated with silver nitrate and measuring the length of black stains.

2.3.3   Choice of Solid Sorbents and Devices

Two general types of sorbent devices that appeared promising were packed tubes and chemically treated filter paper. Of the two, the packed tubes were considered to have greater capacity for contaminant sorption, and were chosen for the initial experiments. Table I presents calculations on the volumes of contaminant gases required for the prescribed sampling conditions. It shows that the sorber must be able to retain 96 liters of contaminant gas at 5 times the TLV; this comes to as high as 5.3 mg in the case of HCN.

With respect to the merits of adsorption vs. chemical reaction, it is considered that chemical reaction to form a nonvolatile species would appear to be preferred unless the adsorbed gases were retained very strongly, which is not usually the case. With these considerations in mind, the following solid state sorbents give promise of being efficient trapping media.

For HF, formation of the fluoride ion by reaction with a strong or weak base appears feasible. A procedure employing sodium bicarbonate packed tubes has been reported [52]. Similar tubes may be useful for F_2.

For HCN, reaction with a strong base to form cyanide ion appears preferable, and a packed tube design should work.

For PH_3 which is a strong reducing agent, an oxidizing material could be used to form a nonvolatile phosphate. Materials such as $AgNO_3$, $KMnO_4$ and other oxidants should trap this gas, with subsequent determination of the stable phosphate.

For Cl_2 a reducing agent can be used as the trapping medium. One possibility is the use of potassium iodide to trap the chlorine, with resultant formation of iodine, a method that is used to determine ozone in air [55]. It might be necessary to determine the total chloride concentration also, to assure that the iodine was formed solely from the Cl_2 and not some other oxidizer present.

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Table 1. Concentration Ranges of Reactive Gases

GAS	M.W. (g/mole)	TLV (ppm)	Conc'n[b] Range (ppm)	Gases Collected[a]		
				4 hr at 50 ml/min (12 liters) (μg)	1/4 hr at 1.0 l/min (15 liters) (μg)	8 hr at 200 ml/min (96 liters) (μg)
HCN	27.03	10	2	27	33	212
			50	663	829	5,300
HG	20.01	3	0.6	6	7	47
			15	147	184	1,200
F_2	38.00	0.1	0.02	0.4	0.5	3
			0.5	9	12	75
Cl_2	70.91	1.0	0.2	7	9	56
			5.0	174	218	1,400
PH_3	34.00	0.3	0.06	1	1	8
			1.5	25	31	200

[a] μg = No. liters x ppm x $\dfrac{M.W.}{24.45}$

[b] Range 1/5 to 5 times the TLV.

These choices, based on the literature review, were considered only as a starting point in the experiments with hydrogen fluoride, phosphine, and hydrogen cyanide. As will be seen in Section 3, the sorber of choice for hydrogen fluoride was sodium acetate, and for phosphine was charcoal or $KMnO_4$ dispersed on silica gel. None of these were mentioned in the literature.

2.4   Gas Analysis

A brief literature review was undertaken to guide the choice of analytical methods and solid sorbers for the gases of interest. It was not intended to trace the history of chemical analysis for these gases or to survey their applications to various different fields of interest. Rather, the survey focused its attention mainly on textbooks and reviews in order to learn which methods were considered so reliable as to be designated "standard" methods. Because of this limited objective the survey did not follow the enormous body of available foreign literature other than to call attention to specific Japanese, Russian, Polish, and Romanian papers of immediate interest.

The collection and subsequent determination of hydrogen fluoride, fluorine, hydrogen cyanide, chlorine, and phosphine have been treated extensively in the literature of the past ten years. An examination of recent review texts, Chemical Abstracts, and Air Pollution Abstracts uncovered considerable work on fluorine, hydrogen fluoride and hydrogen cyanide; and somewhat less information on chlorine and phosphine.

2.4.1   Determination of Contaminant Gases

This review describes the most widely used methods of gas detection and determination as well as the officially recognized methods of analysis. The standard methods which were a logical choice for use with this program, are here defined as those listed in the 1973 Annual Book of ASTM Standards Part 23, "Water; Atmospheric Analysis," [1] or in "Standard Methods for the Evaluation of Water and Wastewater," [2] which will hereafter be referred to as "Standard Methods ..." In at least one case (i.e. phosphine) the standard methods were judged to be awkward for determining contaminant gas on solid sorbers. Less rigorous analytical methods were preferred for their speed and simplicity in the initial evaluations, reserving the standard methods for ultimate calibration and reference analyses later on. In all cases the choices that were made of preferred analytical methods for determining the contaminant gases were based on the information derived from the literature review.

Trace concentrations of gases have been determined mostly by colorimetric techniques, but almost all conceivable methods have been reported: titrations to turbidimetric, color, or amperometric end points, coulometry, gravimetry, gas chromatography, and atomic absorption spectrometry for indirect determination of unreacted metals in solution. Recently, potentiometric determinations using ion selective electrodes have been gaining in popularity [3]. Anion selective electrodes have been reported for fluorine and hydrogen fluoride, cyanide ion, phosphorous (V) ion, and chlorine (hypochlorite ion), the latter not to be confused with chloride [4].

A.   Fluorine and Hydrogen Fluoride Determination

Fluorine and hydrogen fluoride are listed together because they are frequently determined by similar procedures since fluorine is changed to hydrogen fluoride in the presence of moisture in neutral or acid media; also, they can be separated easily by absorbing HF on $NaHF_2$ if they appear together.

ASTM D 3269-73T, available as a preprint of the 1974 edition of reference (1) describes the potentiometric determination of fluorides in the atmosphere by ion selective electrodes using a combined total ionic strength adjuster and buffer (TISAB) containing a complexing agent cyclohexylene-dinitrilotetraacetic acid (CDTA). Older methods such as that described in ASTM D 1179-72 [1] or in "Standard Methods..." [2a] have used citrate as the TISAB.

Colorimetric methods have been standard for fluoride determinations; classically, these have depended on the bleaching of highly colored metal complexes such as Zr-Eriochrome Cyanine R, or Zr-SPADNS as described in ASTM D 1179-72 and ASTM D 3269-73T. The latter reference describes also a relatively new color-forming reaction using La-Alizarin complexone (also called Alizarin Complexan and Alizarin Fluorine Blue).

Ion selective electrodes for fluoride are mentioned favorably in reviews by Lambert (1968) [7a] and by Warner (1973) [8a] as significant new developments in fluoride analysis. Svoboda and Ixfeld (1971) [9] have used an ion selective electrode with citrate buffer to analyze gaseous fluorine compounds, and Hermann (1972) [10] recommends it in his review of methods for measurement of gaseous fluorine compounds in air environments, along with the Alizarin complexone and the Zr-SPADNS spectrophotometric methods. Durst (1969) [11] has used an ion selective electrode to determine fluoride in dusts. Biheller and Resch (1971) [12] and Jahr (1972) [13]

have used fluoride ion selective electrodes for sensitive, routine measurements with sodium formate impregnated solid state absorbers.

Classical spectrophotometric methods for fluorine and hydrogen fluoride have depended on the bleaching of metal-complex color lakes such as Zr-SPADNS or Zr-Alizarin where the metals are removed as stable fluorides, thereby decreasing the color of the solutions. A new standard method (in ASTM D 3269-73T) depends on the formation of the highly colored La- or Ce-Alizarin complexone. This appears to be the first reported reaction in which fluoride ion forms a part of a colored complex. Leithe (1971) [14] discusses this method in considerable detail, and it is also mentioned prominently in Lambert's review chapter [7a] as being suitable down to 0.1 ppm of fluoride ion. West et al. [15] have used the method for determining atmospheric fluorides, as have Marshall and Wood [16], Huygen [17], Desbaumes et al [18], and Hermann [10].

Guilbault (1973) [19] has described fluorometric techniques which measure the decrease of fluorescence of metal-complex reagents such as Al-Acid Alizarin Garnet R, Al-Morin, Zr-3-Hydroxyflavone, and Mg-8-Hydroxyquinoline as the metals are complexed by the fluoride; and also a direct-assay procedure based on the increase of fluorescence of the Zr-Calcein Blue complex.

The classical spectrophotometric methods for fluoride are still to be found in recent compilations and reviews: e.g. Boltz (1973) [8b] describes the Zr-Xylenol Orange, Sr-Chloranilate, and Zr- and Th-Eriochrome Cyanine R procedures and just mentions ion selective electrodes in passing. Other methods for fluorine and hydrogen fluoride include titration with thorium nitrate using alizarin or xylenol orange as indicators as described in ASTM D 1606-60 and ASTM D 3269-73T; gravimetric determination of lithium fluoride [20]; and direct separation and determination by gas chromatography [6b, 21,22].

B. Chlorine Determination

"Standard Methods..." calls iodometry the standard against which other methods are judged, and amperometry as the most accurate method for free chlorine [2b]. The starch-iodide titration is described in ASTM D 1427-68 and the amperometric method in ASTM D 1253-68 and in reference (2b).

A commercially available chlorine electrode (as opposed to chloride) is available for determinations in the 0.01-10 ppm range [4]. No literature references to potentiometric determinations using this electrode were found.

The ortho-Tolidine colorimetric method is the one most frequently used [14]. It is described in detail in ASTM D 1253-58 and in "Standard Methods" [2b]. The latter reference describes other colorimetric methods including those using reagents Ferrous DPD (i.e. N,N-diethyl-p-phenylenediamine), leuco crystal violet; methyl orange; and SNORT (stabilized neutral o-tolidine); and includes a table describing the precision and accuracy of these residual chlorine methods (Appendix A). The table shows the SNORT method to have one of the lowest relative errors among 15 laboratories for determining free residual chlorine in water at the 0.8 ppm level. In contrast, Sakai (1972) [27] says that ortho-Tolidine colorimetry is not good for concentrations below several ppm.

The Methyl Orange method involving the quantitative bleaching of methyl orange by chlorine is reported in recent publications. Thompson et al. (1971) [28] determined 0.05-1.0 ppm Cl_2 by bubbling ambient air directly through the reagent solution. Forwerq and Dopfer (1969) [29] describe an auto-analyzer for measuring chlorine emissions by the bleaching of methyl orange; and two Russian articles, one by Vil'ner (1972) [30] and the other anonymous (1972) [31] mention methyl orange for determining chlorine in air.

Miscellaneous methods for chlorine include micro-coulometry to ±2.5 percent accuracy and requiring no calibration, reported by Dennison and Menichelli (1972) [32], and a Pt-Ag galvanic cell with buffered KI electrolyte, described by Vasak (1972) [33]. Guiochon and Pommier [6] describe gas chromato-graphic separations of chlorine from other gases on columns of silica gel or Chromosorb wetted with fluorocarbon grease or oil.

C. Hydrogen Cyanide Determination

ASTM D 2036-72 [1] describes a standard method for cyanide ion by conversion to cyanogen chloride using Chloramine-T, and subsequent colorimetric determination with pyridine and barbituric acid. Pyridine-pyrazolone colorimetry (after Chloramine-T treatment) has also been listed as a standard method [2c]. Potentiometry using a cyanide ion selective electrode has not been mentioned as a standard method although cyanide electrodes have been available commerically. Mascini (1971) [35] has used a cyanide electrode for measuring air and water pollutants; his recent note on the pH and metal ion sensitivity of this electrode (1973) [36] may explain the absence of a standard potentiometric method for cyanide ion.

In their comprehensive review of available methods for determining cyanide, Bark and Higson (1963) [37] state that colorimetric methods are best in the 0.1-1.0 ppm concentra-tion range. They favor the Chloramine-T conversion of

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cyanide to cyanogen chloride with subsequent color development by either (1) pyridine-pyrazolone or (2) pyridine-benzidine reagent which is banned now because of its carcinogenic nature. Boltz reviews methods for cyanide (1973) [8b] and states that the Konig reaction, on which the Chloramine-T pyridine-pyrazolone method is based, is the most extensively used method for HCN. The method is described in "Standard Methods" [2c] and Epstein (1947) [38] is credited with its development.

Other sensitive methods for cyanide include the Chloramine-T Nicotinamide method of Hanker et al. (1957) [39] which yields a blue fluorescence that permits CN⁻ to be determined between 0.30-5 ppm according to Guilbault [19]. The fluorescent reaction between CN⁻ and p-benzoquinone is specific for cyanide and is sensitive to 0.2 μg in the total volume [8b, 19, 40].

Miscellaneous methods for cyanide that have been reported include the demasking of colored or fluorescent metal chelates by formation of stable cyanide complexes; amperometric silver nitrate titration; polarography; potentiometric titration with Hg_2Cl_2; and gas chromatography.

D. Phosphine Determination

The direct determination of phosphine gas is not treated in the descriptions of standard methods, but there are methods for orthophosphate to which phosphine can be converted. The standard colorimetric methods are based on the formation of molybdophosphates or molybdovanadophosphates, differing in the types of reducing agents employed, as stannous chloride, ascorbic acid, etc. These are described in ASTM D 515-72 [1] and in "Standard Methods" [2d]. Interlaboratory tests [2d,7b] reporting on the precision and accuracy of various phosphorous methods are shown in Appendixes B and C. The Stannous Chloride method seems to give the smallest error.

Berck et al. [5] have described gas-liquid chromatography of phosphine at the ppb level; Guiochon and Pommier [6] describe the gas chromatographic separation of gaseous hydrides including phosphine; and Dumas (1964)[45] has described the determination of phosphine in air down to 0.5 ppm.

Phosphine has been determined as orthophosphate after oxidation in a dilute $KMnO_4$ - sulfuric acid solution. If it is possible to collect phosphine as orthophosphate using a suitable solid sorber, then the standard methods for phosphate can be used. Most spectrophotometric methods for orthophosphate are based on the formation of phosphomolybdenum blue or similar substances. The standard methods [1,2d] and others are reviewed by Boltz [8b], and by Burton (1973) [46] who states that the Ascorbic Acid method now is used in probably

more than 90 percent of analyses. Dechant et al. (1966) [47] use a colorimetric method based on silver diethyldithiocarbamate. Fluorescence methods based on the formation of molybdophosphate-rhodamine B, quenching of Al-morin fluorescence, and an enzyme reaction with glycogen to form NAPDH* have also been mentioned [8b,19].

Other methods for phosphate include potentiometric and conductometric methods based on the release of HCl from $HgCl_2$; turbidimetric methods based on the reduction $AgNO_3$ to Ag°, and the gravimetric determination of $NH_4)_3PO_4\cdot12MoO_3$.

A recently described ion selective electrode for phosphorous (V) claims a measurement range of 0.1-95,000 ppm for phosphoric (V) ion [4]. Potentiometric methods using this electrode have not yet been seen in the literature.

3. EXPERIMENTAL RESULTS

The efficiency of the solid state sorbers for trapping and holding the contaminant gases for subsequent analysis was evaluated by experiments involving passing known concentrations of gases through the solid sorbers into either a liquid trap having essentially 100 percent trapping efficiency (e.g. aqueous 0.1 N NaOH to retain HF) or a solid trap having the same high trapping efficiency (e.g. $AgNO_3$ impregnated silica gel to retain PH_3). Three chemical analyses are of importance here, and all must be carried out precisely and accurately. These are: (1) determination of the steady-state gas concentrations, (2) determination of the amount of gas retained on the solid sorbers, and (3) determination of the gases in the downstream bubbler or trap if any. The analytical procedures were chosen from those deemed most suitable in the literature review.

This section describes the experimental results obtained in sorber studies with hydrogen fluoride, hydrogen cyanide, and phosphine.

3.1 Hydrogen Fluoride

In this chapter, we describe the equipment for generating hydrogen fluoride gas mixtures and for air sampling, the analytical method for fluoride determination, and the selection of solid sorbents. We present the experimental data on collection efficiencies of the various sorbents, temperature and humidity effects, breakthrough, and precision studies. We also provide the specifications on construction of the sorption tubes and a detailed procedure for the analysis of fluoride.

*NADPH is hydrogenated NADP, the sodium salt of triphosphopyridine nucleotide.

3.1.1. Gas Generating and Sampling Systems

The experiments required hydrogen fluoride gas mixtures of several concentration levels and sampling at various flow rates. A gas generating system was constructed to produce hydrogen fluoride-air mixtures of the desired concentration levels, i.e., 1/5 TLV to 5 TLV levels, and also a sampling system to withdraw gas samples at constant flow rates ranging from 50 ml/min to 1 liter/min. Figure 4 is a schematic drawing of the systems.

The gas generating system consisted essentially of two differential flow controllers (one had a stainless steel diaphragm for hydrogen fluoride), two rotameters for measurement of flow rates of air and hydrogen fluoride gas, a stainless steel mixing manifold, and a stainless steel sampling manifold. Either thick-wall Teflon or stainless steel hardware was used wherever hydrogen fluoride gas passed. A bulk mixture of hydrogen fluoride in nitrogen supplied by a gas cylinder was diluted with in-house compressed air in the mixing manifold. Prior to mixing, the air was filtered through glass wool only. Proper adjustment of the two rotameters (valves V-2 and V-4 in Figure 4) produced hydrogen fluoride gas mixtures of the desired concentration levels. The sampling manifold was always open to the atmosphere.

The gas sampling system consisted of a 3-way valve, two sorption tubes in series, a brass in-line filter, a differential flow controller, a rotameter, and a vacuum pump. Gas samples were withdrawn under vacuum from the sampling manifold in the gas generating system. When adjusting valve V-6 (Figure 4) for the proper sample flow rate, the 3-way valve V-5 was opened to the atmosphere. The flow rates of the hydrogen fluoride-air mixtures in the gas generating system were always maintained at three times or more the flow rates of the gas samples in the sampling system. The rotameters were calibrated by a wet test meter.

3.1.2. Selection of Solid Sorbents for Hydrogen Fluoride

Several substances for sorption of hydrogen fluoride in air have been reported in the literature. These have included sodium carbonate, sodium bicarbonate, sodium formate, sodium hydroxide, and potassium hydroxide. In preliminary screening, the collection efficiencies of sodium bicarbonate powders, sodium citrate crystals, activated charcoal, activated charcoal soaked with saturated sodium bicarbonate solution, firebricks soaked with saturated sodium bicarbonate solution, and sodium acetate crystals were determined. These substances were packed in glass tubing of 6 mm outside diameter. The resultant tubes had a maximum pressure drop of 2.54 cm

Figure 4. Gas Generating and Sampling Systems for HF
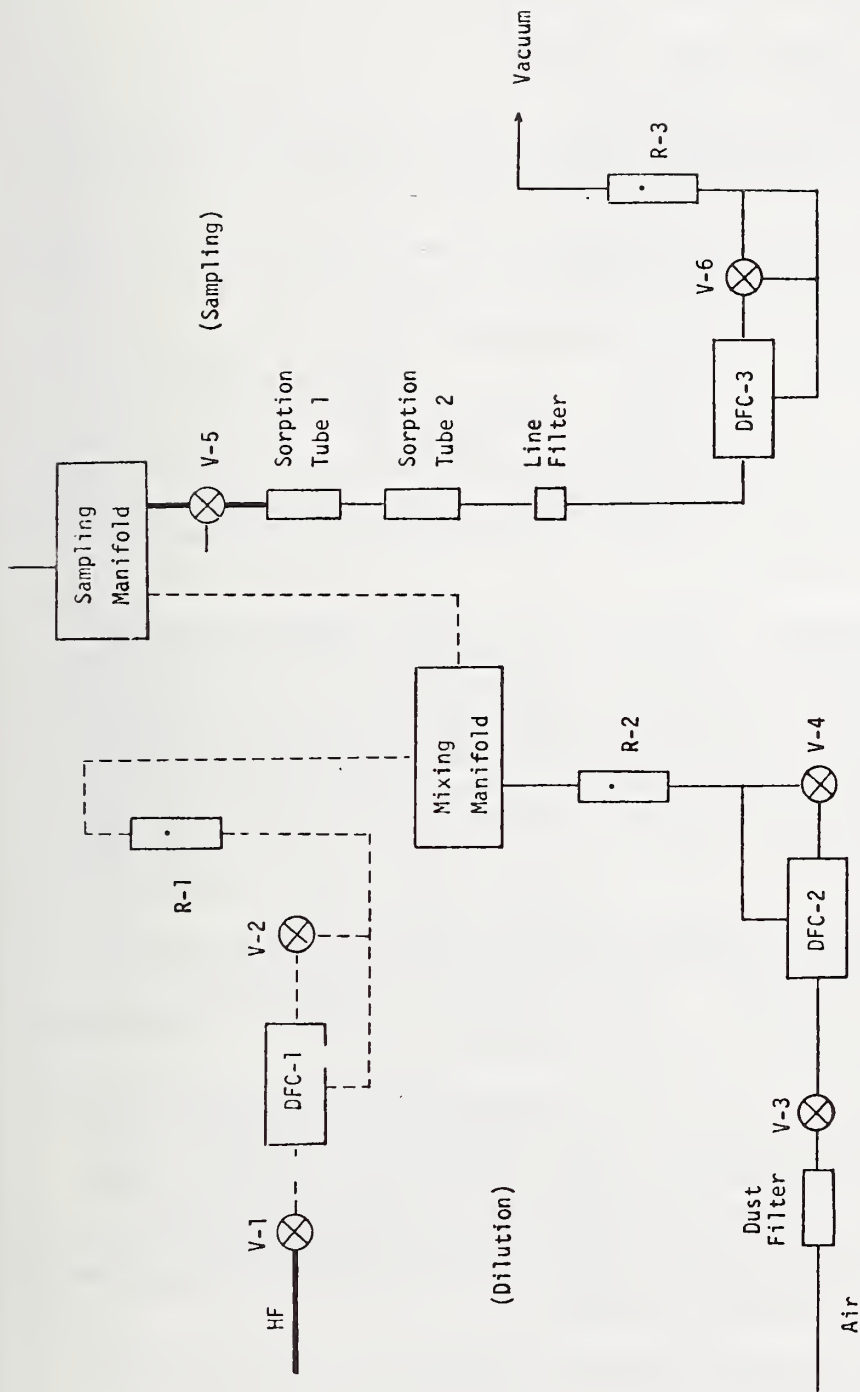
LEGEND:

Tubing: Fine lines 1/4" copper; heavy lines 1/4" Teflon; dotted lines 1/4" stainless steel.
V-1, V-3: Shutoff valves, stainless.
V-2, V-4: Metering needle valves, stainless.
V-5: Three-way ball valve, stainless.
R-1, 2, 3: Rotameter flow meters.
DFC-1, 2, 3: Differential flow controllers.

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Hg at a flow rate of 1 liter/min. Table 2 shows the collection efficiencies of these substances. The collection efficiency, E, is defined as

$$E = \frac{(A_1 - B_1)}{(A_1 - B_1) + (A_2 - B_2)} \times 100 \qquad (1)$$

where A_1 = amount of hydrogen fluoride collected in the first sorption tube, in moles.

A_2 = amount of hydrogen fluoride collected in the second sorption tube, in moles.

B_1 = blank for the first sorption tube,

B_2 = blank for the second sorption tube.

The amount of hydrogen fluoride collected in the sorption tubes was measured by the fluoride selective electrode method as described in Section 3.1.4. The blanks were determined using the ambient air of the laboratory.

Table 2 is a summary of the collection efficiencies of the solid sorbent system studied. Although sodium bicarbonate showed relatively high collection efficiencies, it had the disadvantage that it is available only in the powder form, and the pressure drop of the sorption tube was over 25 cm Hg. Its very low collection efficiency at the flow rate of 50 ml/min indicated that physical adsorption and desorption might have taken place.

It was difficult to leach sodium fluoride from activated charcoal and firebrick substrates. Fine particles were found in the resultant solutions which required filtration before analysis. No attempt was made to determine the recovery of fluoride in the leaching process.

There is evidence that water is desirable for the reactions of the solid sorbents with hydrogen fluoride, as shown by the higher collection efficiency (31.5 percent) of sodium citrate plus 5 percent glycerine in water over the dry salt. Activated charcoal soaked with saturated sodium bicarbonate solution also gave higher collection efficiencies when 5 percent glycerine was present.

The selection of sodium acetate crystals as the sorbent for hydrogen fluoride was made on the following basis:

1. High collection efficiency for hydrogen fluoride,

Table 2. Collection Efficiencies of Various Sorbents for
3 ppm Hydrogen Fluoride Gas

Sorbent	Collection time	Flow rate (ml/min)	Collection eff (%)
NaHCO$_3$	15 min	1050	98.7-99.8[a]
	4 hr	211	96.8
	6 hr	211	95.8
	8 hr	211	99.8
	8 hr	50	73.3
Activated charcoal	15 min	1050	93.1, 97.4
20-40 mesh	6 hr	211	90.7
(MSA, Pittsburgh, Pa.)[b]	4 hr	41	82.8
	8 hr	50	52.5
Firebrick soaked with sat'd NaHCO$_3$ sol'n	15 min	1050	70.6
Charcoal soaked with sat'd NaHCO$_3$ sol'n	15 min	1050	61.0, 85.0
Charcoal soaked with sat'd NaHCO$_3$ sol'n + 5 percent glycerine	15 min	1050	89.0, 90.3
Na citrate crystals (reagent grade) 20-40 mesh	15 min	1050	12.9
	4 hr	211	11.8
Na citrate on polyurethane + 5 percent glycerine sol'n	15 min	1050	31.5
Na acetate crystals (reagent grade) 20-40 mesh	15 min	1050	93.9-97.5[c]

[a]A total of 9 runs.
[b]See disclaimer on p 41.
[c]A total of 6 runs.

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2. Acetate acts as a pH buffer in the fluoride ion selective electrode method of analysis,

3. Ready availability as reagent grade in the 20-40 mesh size,

4. Relatively inexpensive,

5. Chemical stability of both sodium acetate and the reaction product sodium fluoride under normal conditions,

6. Presence of three molecules of hydration per formula weight highly desirable for the reaction with hydrogen fluoride in air,

7. Non-toxic, non-irritating, non-corrosive,

8. High solubilities of both sodium acetate and sodium fluoride in water.

3.1.3. Construction of Sorption Tubes

The sorption tubes were constructed according to the procedure given below. The sodium acetate used in the experiments was pooled from the reagent bottles which were obtained from three different chemical companies. The crystals of 20 to 40 mesh were separated from the bulk in the reagent bottles by sieving. The only apparent difference among these three sources of sodium acetate was in the distribution of particle size. An average of 10 percent of the sodium acetate in the bulk was of 20 to 40 mesh. No attempt was made to determine the distribution of particle size of the 20 to 40 mesh crystals. Figure 5 is a drawing of the sorption tube.

Specifications for Sorption Tubes

1. Join one piece of Pyrex glass tubing of 6 mm outside diameter and 3 cm long to a Pyrex glass tubing of 13 mm outside diameter and 4 cm long. Make a very slight constriction at the joint.

2. Join another piece of Pyrex glass tubing of 6 mm outside diameter and 3 cm long to the other end of the 13 mm tubing above. Make a very slight constriction at the joint.

3. Introduce a wad of loose surgical cotton, about 5 mg, inside the tube.

4. Blow dry air inside the tube to arrest the cotton at the "neck" of the tube.
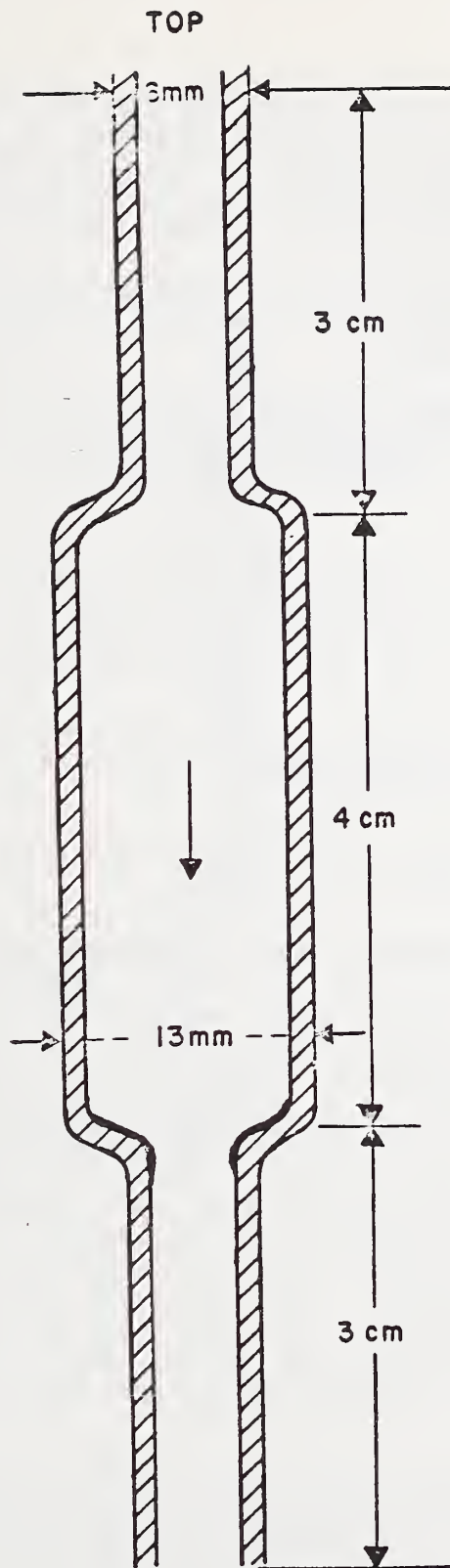
Figure 5. Sorption Tube for HF

5. With the aid of a small funnel and a piece of Tygon tubing, fill the tube with 20 to 40 mesh reagent grade sodium acetate crystals, $NaC_2H_3O_2 \cdot 3H_2O$, up to the "neck". Gently tap the tube to help the crystals settle. Do not use crystals that are lumped together.

6. Insert a wad of loose surgical cotton, about 4 mg, on top of the sodium acetate crystals. Do not press the cotton down.

7. Print an arrow on the outside walls of the tube to indicate the air flow direction, i.e., the same direction as the air that was used in seating the cotton.

8. Connect the sorption tube to an orifice which has an opening to pass air at 1 liter/min. Connect the orifice to a manometer and vacuum with a tee. Figure 6 is a drawing of the pressure drop measurement apparatus.

9. Turn the vacuum on to check the pressure drop. Reject the sorption tubes with a pressure drop of over 2.54 cm Hg.

10. When not in use, place plastic caps on both ends of the sorption tubes.

3.1.4. Analytical Method for Fluoride

The ion selective electrode method for fluoride determination was chosen on the basis of its selectivity for fluoride and simplicity in operation. The necessary equipment in this method included a fluoride selective electrode, a calomel reference electrode, a pH meter with millivolt mode, and a magnetic stirrer. The concentration of fluoride in a sample solution was obtained from the millivolt reading and a calibration curve. The latter was established from a plot of millivolt response versus fluoride concentrations of standard sodium fluoride solutions. The standard solutions were prepared from known weights of dried sodium fluoride dissolved in 0.88 M sodium acetate solution. The procedure for operation of the fluoride selective electrode instrument is given below.

At the conclusion of gas sampling, the amount of fluoride collected in the sorption tube was determined according to the procedure given below. In the preliminary screening of solid sorbents, the sorbents sodium bicarbonate and sodium citrate were dissolved in sodium nitrate solution to give the same ionic strength as the standard solutions. For charcoal and firebrick, the sodium fluoride was leached out from the substrates with 25 ml water.
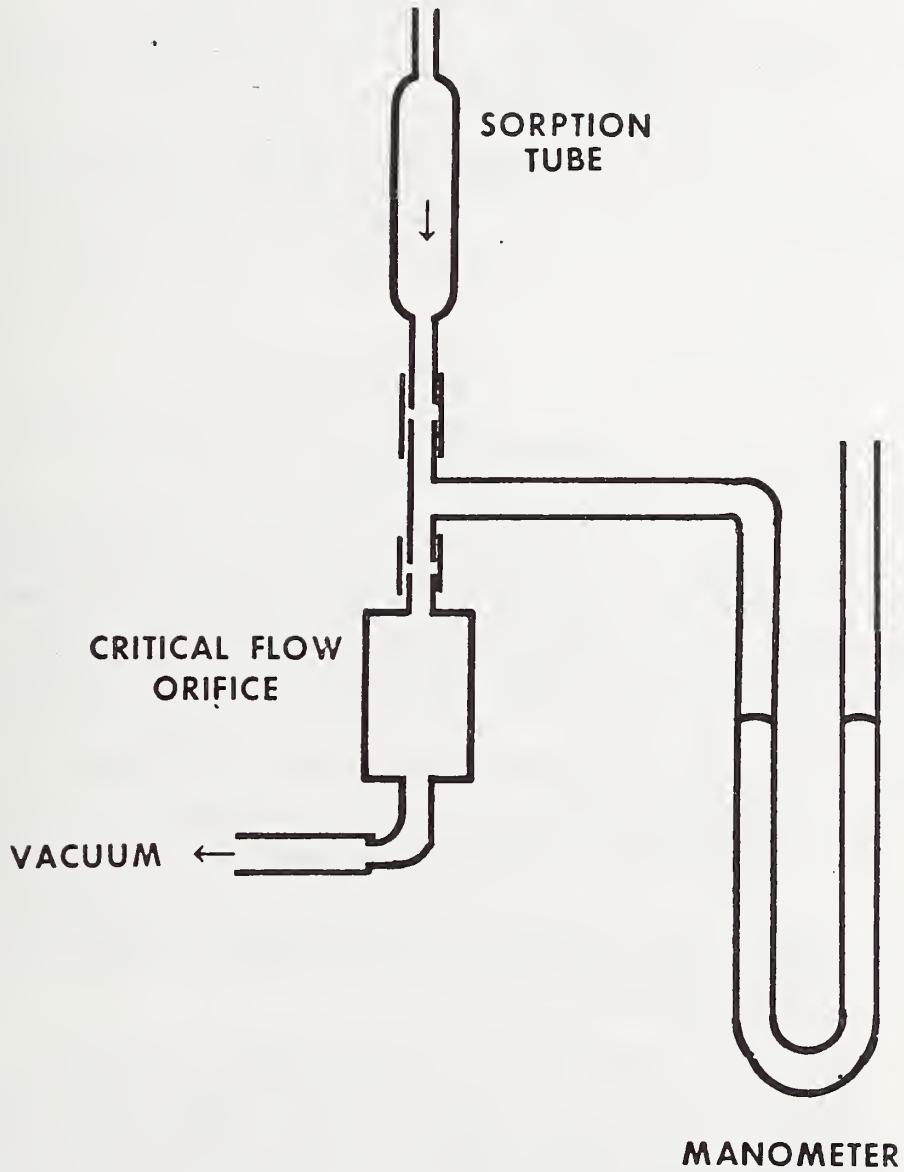
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SORPTION
TUBE

CRITICAL FLOW
ORIFICE

VACUUM ←

MANOMETER

Figure 6. Pressure Drop Measurement Apparatus

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The amount, A, of fluoride collected, in moles of fluoride, was calculated from the following equation:

$$A = \frac{25\ C}{1000} \tag{2}$$

where   A = moles of fluoride in sorption tube

         C = molar concentration of fluoride from analysis of a 25 ml solution

The concentration of hydrogen fluoride, in parts per million (ppm), in the gas samples was calculated from the following equation:

$$\text{ppm HF} = \frac{A \times 24.5}{T \times R} \times 10^6 \tag{3}$$

where T = total collection time in minutes,

         R = flow rate of gas sample in liters per minute at **standard temperature**-pressure condition.

To study the effects of sodium acetate concentration on millivolt response, a series of sodium fluoride standards was prepared in 0.55 M sodium acetate solution. Figure 7 shows the calibration curves of the standard solutions in both 0.88 M and 0.55 M sodium acetate solutions. The effect of sodium acetate concentration was quite insignificant.

Operation of Fluoride Selective Electrode Instrument

1. Connect the fluoride and the reference electrodes to the pH meter. Set the meter to "standby" position.

2. Transfer the sample solution to a 50-ml polyethylene beaker. Add 2 drops of 0.5 N HNO_3 to adjust the pH of the solution to 6.8.

3. Place the electrodes in the sample solution.

4. Place a magnetic stirrer in the beaker and turn on the variable transformer to provide gentle stirring of the solution.

5. At the end of 15 minutes, record the millivolt reading.

6. Set the meter back to "standby" position.

7. Empty the contents of the beaker. Rinse the electrodes thoroughly with distilled water. Wipe the electrodes
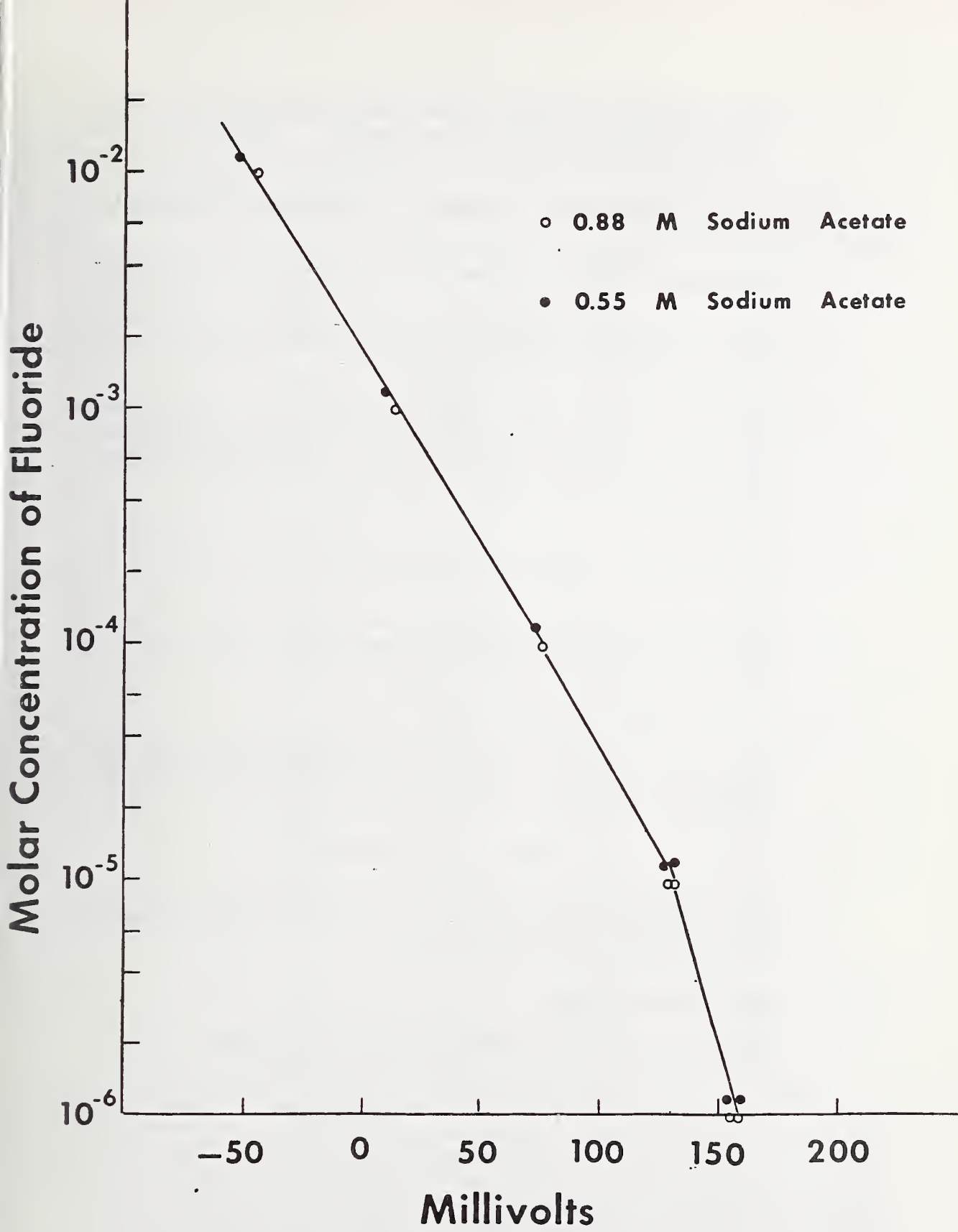
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Figure 7.   Calibration Curve of Fluoride Standard Solutions

dry with soft tissue. The electrodes are now ready
for measurement of another sample. When not in use,
the electrodes should be submerged in distilled water.

Procedure for Measurement of Amount of Fluoride Collected in Sorption Tubes

1. Disconnect the sorption tube from the flow system.

2. Use a pair of straight corrugated forceps to remove
   the top wad of cotton in the sorption tube and place
   it in a polyethylene beaker.

3. Insert the top end of the sorption tube into the neck
   of a 25-ml volumetric flask, and empty the sodium
   acetate crystals into the flask. Gently tap the
   tube against the flask to get the crystals into the
   flask.

4. With a stiff wire, break loose the bottom wad of
   cotton. Let the cotton stay inside the sorption tube.

5. Rinse the inside walls of the sorption tube and the
   cotton with 15-18 ml distilled water. Make sure all
   the rinses go into the flask.

6. Remove the sorption tube.

7. Rinse the cotton in the polyethylene beaker with 5 ml
   distilled water. Add the rinse to the 25-ml volumetric
   flask.

8. Dissolve the sodium salts completely.

9. Add enough distilled water to dilute to 25 ml. Mix
   thoroughly. The solution is now ready for fluoride
   concentration determination.

3.1.5. Experimental Data

A. Collection efficiencies of sodium acetate

Table 3 is a summary of the collection efficiencies of
sodium acetate crystals for hydrogen fluoride at room tempera-
ture (23.9° to 25.5°C). These runs were made in random order
and not in the order as given in Table 3. It was concluded
from these data that 3 gm of sodium acetate crystals of 20 to
40 mesh completely removed hydrogen fluoride from gaseous
mixtures having concentrations of hydrogen fluoride ranging
from 0.5 to 15 ppm, for collection time of 15 minutes at a
flow rate of 1 liter/min, and for collection times of 4 to 8
hours at flow rates of 50 to 200 ml/min.

Table 3. Collection Efficiencies of Sodium Acetate for
Hydrogen Fluoride Gas

Collection time	Flow rate ml/min	ppm HF	g NaAc	Collection eff (%)
15 min	916	4.90	1.87	94.8
15 min	916	5.08	1.87	94.7
15 min	916	3.70	3.0	100
15 min	916	4.64	3.0	100
15 min	916	5.57	3.0	99.7
15 min	1010	0.48	3.0	100
15 min	1010	0.51	3.0	100
15 min	1010	0.57	3.0	100
15 min	1010	0.63	3.0	100
15 min	1010	0.70	3.0	100
15 min	1010	3.54	3.0	100
15 min	1010	15.8	3.0	100
4 hr	52	0.69	3.0	100
4 hr	52	0.74	3.0	100
4 hr	52	0.81	3.0	100
4 hr	52	5.00	3.0	100
4 hr	52	15.2	3.0	100
4 hr	188	4.93	1.87	99.3
4 hr	188	5.11	3.0	100
4 hr	198	0.57	3.0	100
4 hr	198	3.09	3.0	100
4 hr	198	15.4	3.0	100
8 hr	52	0.74	3.0	100
8 hr	52	2.21	3.0	100
8 hr	52	4.64	3.0	100
8 hr	52	16.4	3.0	100
8 hr	188	5.43	3.0	100
8 hr	198	0.57	3.0	100
8 hr	198	4.37	3.0	100
8 hr	198	15.8	3.0	100

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B.   Breakthrough Study and Capacity of the Sorption Tubes

A gas mixture of 15 ppm hydrogen fluoride was passed through two sorption tubes in series at a flow rate of 1.01 liter/min. Every 15 minutes, the second tube was replaced by another sorption tube and its fluoride content analyzed. No breakthrough was observed in 8 hours of collection. The capacity of the sorption tube is therefore greater than 5.8 mg hydrogen fluoride.

C.   Effects of Elevated Temperatures

A Pyrex glass tube 13 mm outside diameter and 25 cm long was placed in front of two sorption tubes, all in series and wrapped with a heating tape. Heat was generated at a constant rate using a variable transformer, and the temperature inside the 25 cm tube was measured by a thermometer with air flowing at 52 ml/min. A hydrogen fluoride gas sample was withdrawn through this assembly at the same flow rate. The experiment was repeated with the heating tape removed and with two new sorption tubes.

Table 4 is a summary of the experimental results for two different collection periods. Together with the experimental data presented in Table 3, it is concluded that the collection efficiency of sodium acetate for hydrogen fluoride was 100 percent at temperatures ranging from 23.9°C to 38.0°C. However, there was a loss of 9 percent of hydrogen fluoride at the elevated temperatures, as shown in the last column in Table 4. Possibly, part of the hydrogen fluoride reacted with the inside walls of the Pyrex tubes before it reached the trapping reagent, resulting in lower absorption than expected.

D.   Effects of Humidity

A bubbler containing distilled water was used to saturate the in-house compressed air with water at 25.0°C. The hydrogen fluoride bulk mixture was mixed with this water-saturated air, and a sample was collected at 1.01 liter/min for 15 minutes through two sorption tubes in series. The experiment was repeated without the bubbler and with two new sorption tubes. The concentration of hydrogen fluoride in the sample was 34.8 ppm based on the dry mixture run.

The collection efficiency in both the water-saturated and dry environments was 100 percent. However, the amount of fluoride recovered in the water-saturated run was only 76.7 percent of that in the dry mixture run. Possibly, part of the hydrogen fluoride reacted with the water vapor, and the product(s) was adsorbed on the inside walls of the mixing and sampling manifolds.

Table 4. Effects of Temperature on Collection
of Hydrogen Fluoride

Temp (°C)	Collection time (hr)	Collection eff (%)	ppm HF	Net mol fluoride collected x 10^{-6}	Ratio of mol fluoride collected (elev temp/rm temp)
36.0	1	100	5.2	0.60	0.91
25.0	1	100	5.2	0.66	
38.0	3	100	22.9	7.98	0.914
25.4	3	100	22.9	8.73	

E. Precision, Bleed-out, Storage, and Shipment Studies

A total of 20 sorption tubes was used to collect hydrogen
fluoride samples under identical experimental conditions, i.e.,
15 minutes of collection time at a flow rate of 1.01 liter/min
and hydrogen fluoride concentration of 3 ppm. These tubes
will be used for precision, bleed-out, storage, and shipment
studies.

Four of these tubes were shipped to NIOSH. Of these four,
two are to be returned at once upon arrival at NIOSH, and the
other two are to be returned one week after arrival at NIOSH.

One of these 20 tubes was flushed with ambient laboratory
air at 25.2°C for 6 hours. Two were kept in a water-saturated
atmosphere at room temperature.

Of the remaining 13 tubes, five will be analyzed at one
time for precision, two will be analyzed one month later, two
will be analyzed one year later, and the last four will be
reserved as spares.

3.2 Hydrogen Cyanide

For the investigation of solid-state sorbents for HCN
it was decided to first determine the concentration of the
contaminant gas by a standard sampling procedure and analytical
method and then to compare these results with the results
obtained with candidate solid-state sorbents. In this way
accurate determinations could be made concerning the efficiency
of collection and the efficiency of desorption of HCN from
solid-state sorbents.

A pressurized cylinder containing 200 cu ft of HCN in
nitrogen with an analyzed concentration of 51 ppm, as received
from the manufacturer, was the contaminant source. For the
experiments described in this section the gas was not diluted
and was delivered to a gas manifold where sampling took place.
The sampling system was of the constant flow type described
in Section 2.2 of this report. For each determination a
total of 15 liters of gas was sampled, at a flow rate of one
liter per minute for a period of 10 minutes.

3.2.1. Determination of HCN Concentration

For the determination of the HCN concentration, a stand-
ard sampling procedure was employed involving the capture of
HCN by bubbling the gas through a 0.1 M NaOH solution.
Several designs of bubblers were investigated and different
collection efficiencies were noted. The most efficient
procedure involved the arrangement of two midget impingers

in series, each containing 10 ml of 0.1 M NaOH. The first impinger has a coarse fritted bubbler stem while the second one was of the standard impinger type. After sampling at a rate of 1 liter/min for 15 minutes the contents of each impinger were transferred to a 25 ml volumetric flask and diluted to mark. The concentration of cyanide was determined using the cyanide ion-selective electrode.

Calibration standards for this electrode were prepared by diluting a stock solution of NaCN with 0.1 M NaOH to give solutions of 10^{-3}, 10^{-4}, and 10^{-5}M cyanide. Millivolt readings were made using a pH meter with a digital readout. The plot of millivolt readings vs. concentration on semilog graph paper gave a straight line. The concentrations of the trapping solutions were then determined by the use of this calibration curve.

It was found that about 95 percent of the total cyanide captured was contained in the first impinger. However, it was discovered that the concentration of the HCN was 1 ppm instead of the expected 50 ppm, as the supplier had indicated*.

3.2.2. Screening of Solid-State Sorbents

Although the HCN concentration was below the level needed for this project, it was decided to use this gas to obtain preliminary data on solid-state sorbents.

Two solid-state sorbents, activated charcoal and Ascarite were tested for trapping efficiency. The charcoal tube was of the type developed by NIOSH for trapping organic vapors in air. The Ascarite tube was also of similar design, 6 mm OD and containing a 40 mm length of 20-30 mesh Ascarite.

For these determinations the tube was positioned in the stream of contaminant gas with a midget impinger (bubbler type) downstream from the tube. After sampling, the tube contents were extracted with NaOH, filtered, and diluted to 25 ml. The contents of the impinger were also diluted to 25 ml. Cyanide determinations were made on both solutions.

Activated Charcoal: The average of four determinations
(20-40 mesh)   show the following:

    1.   Based on total cyanide recovered, the charcoal trapped 80 percent and the bubbler 20 percent.

    2.   The total cyanide recovered, however, was 60 percent of the predicted amount.

*See disclaimer on p 41.

Ascarite: The average of four determinations show the
(20-30 mesh) following:

> 1. Based on total cyanide recovered, the
>   Ascarite trapped 100 percent.
>
> 2. The total cyanide recovered, however, was
>   85 percent of the predicted amount.

3.2.3. Discussion

·· It is seen that the charcoal tube shows breakthrough even
at the 1 ppm concentration level; hence, this particular tube
would not be suitable for HCN. However, it should be noted
that a larger charcoal tube may provide sufficient capacity
for HCN. Tubes of this type will be investigated. On the
other hand, the 6 mm Ascarite tube is an effective trapping
agent for HCN.

The recoveries of cyanide from both the charcoal and the
Ascarite tubes, however, were not quantitative. This may be
due to the fact that the extractions were done at room
temperature.

3.2.4. Future Work

Further work will be done with the Ascarite tube and the
wider design charcoal tube. More vigorous extraction proce-
dures will be tested. Other solid-state sorbents will also
be investigated. Arrangements have been made with the manu-
facturer to receive a replacement cylinder of HCN at the
required 50 ppm concentration level.

3.3 Phosphine

Phosphine supplied as 4.5 ppm in nitrogen in a compressed
gas cylinder was delivered to a vacuum sampling system in
an apparatus similar to that previously described for hydrogen
fluoride. The gas was fed through a rotameter into a plenum
from which it was sampled into solid state sorbers at atmos-
pheric pressure by aspiration through a constant-flow
regulator; a sub-atmospheric reference pressure was supplied
by a rotary-vane pump. The strongly reducing nature of
phosphine imposed no limitations on materials of construction
which were glass, brass, Teflon, and neoprene. The flow
system is diagrammed schematically in Figures 2 and 3.

3.3.1. Experimental Method

Promising solid sorbers were screened rapidly to study
qualitatively the ease with which phosphine could be

immobilized in collection devices. The sorbents were packed into two sizes of glass tubes: 6 mm OD as supplied in commercially available charcoal-filled tubes used for collection of organic vapors, and 13 mm OD tubes fabricated in this laboratory and described in the section on Hydrogen Fluoride. The tubes were filled to a depth of 50 mm except the 6 mm tubes which were used as received with 30 mm of charcoal inside.

A plug of silver nitrate-impregnated silica gel was inserted in the base of each tube to signal phosphine breakthrough, denoting the end of each experiment. This material was prepared by slurrying 65 g of silica gel with 100 ml of 1.5 percent $AgNO_3$ solution, stirring manually on and off for 15 min, pouring off the excess liquid, and drying for 4 hr at 90°C.

The sorber materials studied were:

1. Silica Gel (W. R. Grace Type 15, 30 - 60 mesh).*

2. Silica Gel impregnated with silver nitrate.

3. MSA Charcoal tubes (as used for organic vapors).

4. Activated Charcoal (Pittsburgh Type OL 20 - 50 mesh).*

5. Potassium permanganate, reagent grade.

6. Silica gel impregnated with potassium permanganate.

Potassium permanganate impregnated silica gel was prepared in the same manner as silver nitrate silica gel using 1 g of $KMnO_4$ and 50 g silica gel (6 - 16 mesh).

The sorber tubes were either straight 6 mm OD tubes constricted at one end, or 13 mm OD tubes 80-90 mm long with 6 mm OD end pieces to permit them to fit into the plenum and the tubing connectors. When filled to a depth of 50 mm they contained about 3 g of material. Glass wool plugs held the sorber material and the silver nitrate-silica gel indicator in place for most of the experiments but the 50 mm pressure drop across the filled tubes exceeded the specifications which called for no more than 25 mm pressure drop at a flow of 1 liter/min. When a thin polyester felt was substituted for glass wool, the pressure drop across a filled charcoal tube with silver nitrate-silica gel indicator was only 20 mm of mercury at 1 liter/min.

The sorber tubes were inserted into the plenum chamber in which 4.5 ppm (nominal) phosphine in nitrogen flowed at
*See disclaimer on p 41.   37

a rate of 2.1 liter/min, and the gas was sampled at a controlled
rate of 1.0 - 1.4 liters/min. The time for the gas to break
through to the bottom of the sorber tubes, as signalled by
immediate blackening of the silver nitrate silica gel was an
indication of the ability of the sorber materials to immobilize
phosphine.

3.3.2. Experimental Results

Table 5 summarizes the data obtained to date. The break-
through experiments indicate that solid sorbers which depend
on physical adsorption have a limited but still useful capacity
for retaining phosphine. Silica gel is clearly unsuitable
by itself. On the other hand, activated charcoal in a 13 mm
dia. column containing about 2 g of material is capable of
retaining 34 liters of phosphine at 4.5 ppm (nominal), about
15 times TLV. This capacity is suitable for the 12-liter
collection at 50 ml/min and the 15-liter collection at 1.0
liter/min; and diluted 3:1 to make a 5 times TLV mixture the
capacity comes to 3 x 34 = 102 liters, just exceeding the
96-liter requirement for the 8-hr collection at 200 ml/min.

The immobilization of phosphine by reaction with a suit-
able reagent to yield a nonvolatile material appears to be
much more efficient than physical adsorption. Silver nitrate
impregnated silica gel used as the breakthrough indicator func-
tioned very well as a sorber even in the small diameter 6 mm
tubes. The breakthrough time of 43 min. was estimated after
a 17-minute experiment by observing that the black band had
travelled 20 mm and had a total of 50 mm to go. The 43-liter
capacity of the 6 mm tube would be quadrupled by using a 13 mm
tube, but even the small tube exceeds the specified sorption
requirements considering that the phosphine gas concentration
is 15 times TLV.

The choice of potassium permanganate as a sorber was
based on its ability to form nonvolatile ortho-phosphates, so
it was expected that $KMnO_4$ would be an excellent sorber. This
turned out to be true, but surprisingly it was not the
crystalline $KMnO_4$ that functioned well, but the $\overline{KMnO_4}$ on
silica gel, present at a concentration of only about 16 mg
$KMnO_4$ per gram of silica gel. Apparently moisture is required
for the oxidation to proceed, and the roughly 30 percent
moisture content of the silica gel is necessary for the
reaction. No breakthrough was observed after 31 min flow at
1.3 liters/min.

Desorption experiments carried out on the permanganate-
coated silica gel showed that the color could be removed
completely after several extractions with water. No desorption
experiments were carried out on charcoal, to date.

Table 5 . Phosphine Sorption on Solid Materials[a]

Sorber (mesh size)	Column size	Sorber Weight (g)	Sampling rate (l/min)	Time for breakthrough	Liters Sorbed
Silica gel (30-60)	50 mm in 13 mm tube	3.0	1.0	20 sec	- -
Silica gel (30-60)	120 mm in 6 mm tube	- -	1.0	30 sec	- -
AgNO₃ on Si gel	50 mm in 6 mm tube	- -	1.0	43 min[b]	43[b]
MSA charcoal tube	30 mm in 6 mm tube	- -	1.0	20 sec	- -
Charcoal (20-40)	50 mm in 13 mm tube	1.9	1.4	24 min	34
Charcoal (20-40)	75 mm in 13 mm tube	2.5	1.0	34 min	34
KMnO₄ crystals	50 mm in 13 mm tube	5.9	1.0	4 min	4
KMnO₄ on Si gel	50 mm in 13 mm tube	3.4	1.3	No breakthrough[c] to 31 min	40

[a] Phosphine 4.5 ppm (nominal) = 15 times TLV.

[b] Estimated breakthrough time from rate of travel of black stain, about 1 mm per minute. Experiment terminated after 17 min (20 mm stain) to save phosphine gas.

[c] Experiment terminated after 31 min to save phosphine gas. Sorption capacity expected to be high, by analogy to AgNO₃ on silica gel.

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3.3.3.   Conclusions and Future Plans

The experimental work to date shows that activated char-
coal and permanganate coated silica gel are the foremost
candidates for inclusion in solid sorption devices. The
choice between these, if a choice must be made, will depend
on the ease with which the phosphine may be desorbed and
determined quantitatively. This is the next step of the
experimental program.

Although the silver nitrate impregnated silica gel was
demonstrated to be an excellent sorber, the determination of
phosphine as metallic silver or as insoluble silver phosphate
appears to be very difficult. Consequently it is planned
to use this material only as a visual indicator and to
destroy excess phosphine.

Future plans include the quantitative determination of
phosphine on charcoal by desorption with pyridine and
spectrophotometric measurement of a suitable color reaction
in pyridine, e.g. silver diethyldithiocarbamate as described
by Dechant, Sanders, and Graul [47].

Phosphine on $KMnO_4$ may be present as the ortho-phosphate,
by analogy with the known oxidation of phosphine with aqueous
acid permanganate [47]. If this turns out to be the case, phosphate
can be determined by a standard colorimetric phosphomolybdate
method after destruction of the excess $KMnO_4$.

It is anticipated that the phosphine experiments can be
concluded rapidly after the routine chemical analyses are set
up.

4.   SUMMARY AND CONCLUSIONS

A methodology has been developed for handling and sampling
contaminant gas mixtures at the rates and concentrations speci-
fied. Compressed gas cylinders containing the contaminant
gases at 5 to 15 times the TLV deliver the required gases (after
dilution if necessary) to a constant-flow sampling system which
assures precise metering of the gases through tubes of solid
sorbent into liquid backup traps (if required). Three complete
instrument assemblies have been designed and built for work
with hydrogen fluoride, hydrogen cyanide, and phosphine.

Analytical techniques for determining the amounts of con-
taminant sorbed by the tubes have been developed, based on
reliable methods described in the literature but modified for
the specific applications at hand. Hydrogen fluoride and
hydrogen cyanide are determined by ion selective electrodes.
Phosphine is detected at present with silver nitrate impreg-

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nated silica gel, and spectrophotometric determination using silver diethyldithiocarbamate in pyridine is just now getting under way.

Solid sorbents have been tested on filter paper and in glass tubes 6 mm in diameter (the size used for charcoal sorption of organic vapors in air), and 13 mm in diameter. The latter size of tube proves to contain sufficient sorbent for retaining the required quantities of hydrogen fluoride and phosphine, packed so that the back pressure does not exceed 25 mm Hg at a flow of 1 liter/minute.

The sorbents tested have included firebrick, glass beads, charcoal, silica gel, sodium hydroxide, sodium citrate, sodium bicarbonate, sodium acetate, Ascarite, potassium permanganate, and silver nitrate both in bulk form and dispersed on substrates of filter paper and on silica gel. This choice of sorbents to be tested was based on a literature review of sorbents used in atmospheric analysis of the 5 contaminant gases of interest. To date, sodium acetate proves to be a highly efficient sorber for hydrogen fluoride, while potassium permanganate on silica gel shows considerable promise for phosphine sorption, and Ascarite for hydrogen cyanide sorption. The final selection of PH_3 and HCN sorbers awaits the completion of the quantitative analyses to show the efficiency of the desorption process.

The sorption efficiency of 3.0 g sodium acetate for hydrogen fluoride is 100 percent at all specified flow rates (1.0, 0.2, and 0.05 liters/min), concentrations (1/5 to 5 times TLV), and collection times (15 min to 8 hr). The efficiencies of charcoal and permanganate-coated silica gel for phosphine, and of sodium hydroxide for hydrogen cyanide are in process of measurement.

The feasibility of constructing small, efficient sampling devices containing solid state sorbers to collect contaminant gases for subsequent laboratory analysis has been demonstrated. Future work will include the completion of accurate quantitative determinations of hydrogen cyanide and phosphine sorption, and the evaluation of suitable sorbers for fluorine and chlorine.

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Appendix A

Method	Residual Chlorine Concentration		Number of Laboratories	Relative Standard Deviation %	Relative Error %
	Free µg/l	Total µg/l			
Iodometric		840	32	27.0	23.6
		640	30	32.4	18.5
		1,830	32	23.6	16.7
Amperometric	800		23	42.3	25.0
		640	24	24.8	8.5
		1,830	24	12.5	8.8
Orthotolidine	800		15	64.6	42.5
		640	17	37.3	20.2
		1,830	18	31.9	41.4
Orthotolidine-arsenite	800		20	52.4	42.3
		640	21	28.0	14.2
		1,830	23	35.0	49.6
Stabilized neutral orthotolidine	800		15	34.7	12.8
		640	16	8.0	2.0
		1,830	17	26.1	12.4
Ferrous DPD	800		19	39.8	19.8
		640	19	19.2	8.1
		1,830	19	9.4	4.3
Leuco crystal violet	800		17	32.7	7.1
		640	17	34.4	0.9
		1,830	18	32.4	18.6
Methyl orange	800		26	43.0	22.0
		640	26	30.1	14.2
		1,830	26	19.9	7.2

Appendix B

Method	Phosphorus Concentration			No. of Laboratories	Relative Standard Deviation %	Relative Error %
	Ortho-phosphorus phosphate µg/l	Poly-phosphate µg/l	Total µg/l			
D. Vanadomolybdate	100			45	75.2	21.6
	600			43	19.6	10.8
	7,000			44	8.6	5.4
E. Stannous chloride	100			45	25.5	28.7
	600			44	14.2	8.0
	7,000			45	7.6	4.3
F. Ascorbic acid	100			3	9.1	10.0
	600			3	4.0	4.4
	7,000			3	5.2	4.9
Hydrolysis + vanadomolybdate		80		37	106.8	7.4
		300		38	66.5	14.0
		3,000		37	36.1	23.5
Hydrolysis + stannous chloride		80		39	60.1	12.5
		300		36	47.6	21.7
		3,000		38	37.4	22.8
Persulfate + vanadomolybdate			210	32	55.8	1.6
			990	32	23.9	2.3
			10,230	31	6.5	0.3
Sulfuric-nitric acids + vanadomolybdate			210	23	65.6	20.9
			990	22	47.3	0.6
			10,230	20	7.0	0.4
Perchloric acid + vanadomolybdate			210	4	33.5	45.2
			990	5	20.3	2.6
			10,230	6	11.7	2.2
Persulfate + stannous chloride			210	29	28.1	9.2
			990	30	14.9	12.3
			10,230	29	11.5	4.3
Sulfuric-nitric acids + stannous chloride			210	20	20.8	1.2
			990	17	8.8	3.2
			10,230	19	7.5	0.4

Appendix C

Summary of Data on Phosphate 7b/

Method	No.	Mean	Std. Dev.	Mean Error	Relative Std. Dev.	Relative Error
Sample 1, 10.0 mg., liter						
Stannous chloride	33	9.50	0.816	0.50	8.5	5.0
Aminonaphthol-sulfonic acid	18	9.16	0.374	0.84	4.0	8.4
Stannous chloride with extraction	4	9.19	0.448	0.81	4.8	8.2
Autoanalyzer	5	9.50	0.401	0.50	4.2	5.0
Sample 2, 5.0 mg., liter						
Stannous chloride	33	4.81	0.515	0.19	10.7	3.8
Aminonaphthol-sulfonic acid	20	4.79	0.635	0.21	13.2	4.2
Stannous chloride with extraction	6	6.07	2.830	1.07	46.6	21.2
Autoanalyzer	5	4.45	0.168	0.55	3.7	11.2
Sample 3, 0.5 mg. liter						
Stannous chloride	32	0.52	0.099	0.02	19.1	4.0
Aminonaphthol-sulfonic acid	20	0.65	0.314	0.15	48.3	30.0
Stannous chloride with extraction	6	0.76	0.258	0.26	33.9	52.0
Autoanalyzer	5	0.51	0.195	0.01	38.3	2.0

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15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

A program is described for evaluating the efficiency of solid sorbers for collecting trace quantities of hydrogen fluoride, phosphine, hydrogen cyanide, chlorine, and fluorine in work atmospheres for subsequent laboratory analysis. The gas handling and sampling instrumentation is described, and experimental results to date are presented.

Sodium acetate is a very efficient sorber for hydrogen fluoride, and its solubility in water proves to be highly advantageous for subsequent HF determination by ion selective electrode. Potassium permanganate impregnated silica gel sorbs phosphine effectively, and Ascarite has been found to sorb hydrogen cyanide, but quantitative experiments on the latter two systems are still in progress.

Work on chlorine and fluorine systems will be initiated in the near future.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Air analysis; air sampler; charcoal; chlorine; fluorine; gas analysis; hydrogen cyanide; hydrogen fluoride; industrial hygiene; phosphine; sodium acetate; sorber, solid; work atmosphere

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