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PART I

GENERAL PRECAUTIONS AND TECHNIQUES

1. Physical Precautions

1.1 Homogeneity of the Sample— No analytical result regardless of the accuracy and precision of the procedure can be any better than the quality of the sample submitted for analysis. Therefore, the primary concern of the investigator must be directed to the collection of representative samples and the homogeneity of the air mixtures employed to calibrate both the collection and analytical systems. Human sensory perceptions cannot guide the uninitiated with respect to variations of contaminant concentrations in either space or time. Almost without exception gaseous components are either colorless or are present at such low concentrations as to be effectively colorless. The human sense of smell is notoriously deceptive with respect to concentrations of even highly odoriferous components, therefore, cannot be relied upon for estimating relative quality or uniformity of the ambient atmosphere (2, 4-Part V, 9).

The source of the contaminant, air flow direction and velocity whether due to wind or thermal gradients, density of the contaminant, intensity of sunlight, time of day, presence of obstructions such as trees, buildings, partitions, machinery, etc., which act as baffles to produce turbulence, humidity, and half-life of the contaminant together determine the concentration at any given location. That the concentration can vary by several orders of magnitude within a relatively short radius from the point of reference has been amply confirmed by many investigators. Air may flow either in a stream line or turbulent flow and this factor alone can determine the dispersal pattern of the pollutant (2, 3, 5, 9).

The density of the pollutant in many cases will counteract diffusion processes to an extent which will establish stratification. This phenomenon prevails in the case of many highly toxic and irritant gases such as phosgene, mustard gas, lewisite, chlorine, etc. (5). Natural convective circulation and diffusion in confined spaces such as silos, coal mines, wells, coves, tanks, etc., is not sufficient to maintain a normal atmosphere containing approximately 21 per cent oxygen.

The location of sampling sites whether on a temporary or "grab" sample basis or on a fixed station basis for continuous monitoring over long periods of time is often critical and will determine the validity of the conclusions drawn from the results (1, 2, 3, 9). In the vicinity of industrial atmospheres the variability may be sufficiently extreme to vitiate the results from fixed station monitors regardless of the care taken in locating the samplers. In an alkyl lead manufacturing facility, for example, no relationship could be established between exposure as indicated by urinary lead excretion and numerous fixed station samplers. In this case, correlation was not established until the monitors in the form of a small filter—microimpinger assembly—were actually worn during the entire 8 hr shift by the workmen assigned to these areas (1).

Several excellent treatises have been published on planning the air pollution survey and the effects of meteorological and geographical conditions on the validity of the results. This subject is outside of the field of General Techniques and Precautions; therefore, the reader is advised to consult one or more of these publications for full details (2, 3, 6, 7, 8, 9, 37, 38).

On a smaller scale, even greater care is required to establish uniform mixtures of pollutants in air for use as calibration mixtures whether the system be dynamic or static in principle. Passage through lengths of small diameter tubing to ensure turbulent mixing is one relatively simple expedient for dynamic mixing (11). Other systems employ some form of baffled chamber inserted between the mixing ports and the delivery point (13). Rotating paddles or even loose pieces of sheet metal or plastic (PTFE) to be activated by shaking have been inserted in containers for static mixtures for mixing by turbulence (14). Probably a more effective alternative is to evacuate the container then mix the contaminant with the air at a uniform rate as it is released into the void (14). (Inject from a hypodermic syringe through a needle inserted through a septum). Diffusion alone cannot be relied upon to produce a homogeneous mixture in most cases.

Other effects such as container wall adsorption, humidity, volumetric errors, etc., discussed elsewhere in this section must be recognized and appropriate precautions taken to avoid concentration errors derived from these seemingly extraneous sources when attempts are made to produce homogeneous, known concentrations for calibration purposes.

1.2 Adsorption effects on container walls and connecting tubes—Failure to recognize adsorption effects can lead to serious errors in both collection of samples and in preparation of calibration mixtures especially in static systems. Losses of analyte can occur either by primary adsorption which may be reversible in response to pressure or temperature changes or by secondary adsorption which may involve chemical reaction with another material previously adsorbed (2, 4, 10). The affinity of glass for water, nitrogen dioxide, benzene, aniline, the isocyanates, etc.,

has been recognized (11, 15, 16, 35). The interior surface of a 5-gallon borosilicate glass carboy can adsorb as much as 50 per cent of the benzene in the 100–200 ppm range from a calibration mixture in air within 30 min after preparation. These losses to some extent can be reduced by preconditioning at a concentration higher than the working level but desorption may contribute positive errors (Table 1). Losses by adsorption of polynuclear aromatic compounds on glass have also been reported (17).

This adsorption effect can be minimized in the case of collection of air samples in evacuated glass flasks (Shepherd flasks) or sampling tubes by the introduction of a suitable solvent for the vapor, such as isooctane for benzene and xylidine, directly into the container with thorough rinsing of the inner surfaces (35). In some cases such as the analysis for nitrogen dioxide the solvent or reagent is introduced before the sample is taken e.g., 100 ml sample drawn into a syringe containing 10 ml of Saltzman's reagent (18).

Nitrogen oxides are so tenaciously adsorbed on glass surfaces that rinsing all collecting and analytical glassware with Saltzman's reagent has been found necessary to obtain reliable results. Adsorption of isocyanates on glass, metal or plastic surfaces occurs to such a degree as to preclude preparation of static calibration mixtures even under strictly anhydrous conditions (11).

Positive errors can be included when evacuated double entry gas sampling tubes (fitted with 2 stopcocks) are used for sample collection (10, 19). In this case, after release of the vacuum, additional sample is drawn through the tube for three minutes before closing the stopcocks. Recovery of xylidine increased to 120 per cent in the 50–70 ppm range under these conditions. This error was increased to 40 per cent by adding glass beads to the sampling flask to increase the surface area (35). These

conditions can be avoided by collection of the pollutant in an impinger assembly (Greenburg-Smith, midget or micro).

In dynamic systems prolonged equilibration is required before dependable calibration can be assured. Calibration of toluene diisocyanate (TDI) in the TLV range required passage of the air-TDI vapor mixture through a mixing chamber composed of a 6' length of $\frac{1}{4}$ " copper tubing under strictly anhydrous conditions for 60–72 hr to reach equilibrium. This phenomenon was not entirely produced by the film of water normally adsorbed on the inner walls of the tubing as the system had been carefully heated under vacuum to remove volatile impurities before use (11).

Adsorption is a critical factor in making up standard mixtures for phosgene calibration at concentrations below 1 ppm even after meticulous removal of the adsorbed water film. The use of metal cylinders especially must be avoided. In the development of a continuous monitor for phosgene concentrations below 5 ppm decomposition in metal (steel, stainless steel, copper, aluminum, etc.) or glass tubing was found to be so extensive that their use in the sampling system could not be considered. In this case polyethylene tubing was acceptable. Water adsorbed to the contact surfaces was probably responsible for the losses as HCl was observed to be a by-product. Catalytic decomposition on anhydrous surfaces cannot be ruled out, however (20).

In a study of the efficiency of midget and micro-impingers by collection of aniline from air, losses by adsorption in the glass batch-type generator (5–15 per cent in the 100 μ g range) was encountered unless the system was heated to 60 C in a hot water bath. Even greater were losses due to absorption by gum rubber tubing. Even 3-inch connections introduced significant errors (10 per cent loss) but the losses were

not entirely proportioned to hose length. These losses increased as the age and number of uses increased e.g., recoveries decreased from 83–57 per cent over a period of 8 days (21).

Failure to recognize the effect of adsorption on container walls delayed the determination of the half-life of SO₂ during a study of the fate of SO₂ in the atmosphere at Syracuse University. The half-life was found to be unexpectedly short even after correction for adsorption effects (22).

Tubing through which high concentrations of tetraethyl lead vapor have been drawn will become a source of contamination when "clean" air is passed through the system. These effects are eliminated by use of all-glass systems connected by standard taper, ball joints, "O" ring seals or polytetrafluoroethylene (Teflon) compression connectors.

The adsorption of traces of analytands from liquid solution onto container walls is probably somewhat more widely recognized but certainly requires review to re-emphasize the importance of this source of errors. Heavy metal ions, especially lead, mercury (25), silver (23, 24), cadmium, and antimony, are readily adsorbed by glass and in some cases by plastic surfaces. Lead in urine specimens, for example, is adsorbed to an extent sufficient to introduce significant errors after storage for more than 3 days in borosilicate glass specimen bottles (26). This effect probably is produced by bacterial fermentation which elevates the pH by ammonia release, and co-precipitation of lead with calcium and magnesium phosphates on the glass. In the early stages the precipitate is invisible but nevertheless may contain a significant fraction of the total lead in the sample. In many cases these losses can be held within tolerable limits by reducing the pH to 2 or less with nitric acid. This adsorption loss can be a critical factor in the storage of standard reference solutions and must

be taken into account when collaborative testing programs are set up. Efforts to prepare stable aqueous standardizing solutions of metallic mercury met with failure unless excess mercury remained in contact with aqueous phase. Furthermore, centrifugation is necessary to remove dispersed microdroplets (or HgO) if shaking is employed to accelerate saturation, and a relatively large temperature coefficient of solubility must be taken into account. In spite of these limitations this saturated aqueous mercury solution can be employed as a convenient source of mercury for calibration by comparing recovery from a collecting system with direct analysis of the standard (25).

Filtration of samples collected in a liquid medium should in all cases be avoided if the desired contaminant is to be recovered quantitatively in the liquid phase. Not only will the contact surfaces of the filter funnel and the filtrate receiver adsorb trace materials, but the filter medium (paper, membrane, asbestos mat, glass fiber, micro metallic, etc.) may be highly adsorbant (17). Also, the insoluble fraction removed may retain the analyte as in the case when calcium phosphate is separated from a mixture containing traces of soluble lead compounds (27).

The problem of adsorption on glass surfaces previously discussed requires re-emphasis in the case of porous glass used either as a filter for particulate matter or as a diffuser for collection in liquid absorption systems. Filtration of aqueous solutions of phenanthrene, naphthalene, pyrene or anthracene through a porous glass plate reduced the hydrocarbon concentration as much as 40 per cent (17). When ultraviolet (UV) absorption is employed for analysis, errors from background absorption produced from UV absorbing materials leached from the filters and light scattering from suspended particles must be taken into account (28). A base-line

technique for correction is often required as the solute often alters the light scattering and sedimentation properties with the result the reference blank and the sample are no longer exactly comparable. If removal of sediment is necessary, filtration through polytetrafluoroethylene (PTFE) mat or decantation after centrifugation will minimize losses. In any case, potential losses at each step must be recognized and quantitated.

Rust, scale and other metallic corrosion products can introduce serious errors through adsorption of air pollution components and should be meticulously scoured out of systems used for air sampling, storage or analysis. Many of these oxidation and corrosion products are highly catalytic as illustrated by the rate at which alkyl lead compounds are oxidized by hydrated iron and bismuth oxides (29). Pipe dope used on threaded connections and oils used in cutting threads or lubricating moving parts also can present significant reversible absorption effect. Polytetrafluoroethylene (PTFE) ribbon thread sealant which has a very low absorption coefficient is recommended for threaded joints which require lubrication. Moving parts machined from PTFE are self-lubricating and can be sealed with modified PTFE "O" rings.

The reverse effect has been encountered also. The diffusion of HF in Conway dishes is enhanced ten-fold when silicone grease is used as a sealant for the dual concentric chambered dish cover. Fluoride can be removed quantitatively from aqueous HCl by gentle boiling in the presence of silicone fluid (30).

Adsorption of a secondary layer on container walls may completely alter the character of the surface presented to the collection and analytical system. Soaps and synthetic detergents are especially troublesome in this respect. The film of soap on glass is not removed by

5 per cent trisodium phosphate, chromic acid cleaning mixture, or concentrated nitric acid. Only by baking out in an annealing furnace can "chemical sterility" be achieved. In the colorimetric determination of aromatic nitro and amino compounds in air, this soap film reacts with the color generating reagents. These adsorbed layers appear to retain nitrous acid or nitrogen oxides in a state which does not react with starch-iodide indicator or sulfamic acid but does react with the coupling agent (1-naphthyl 2-ethylenediamine or Chicago Acid) to produce a deep orange color. This spurious color reaction produces high results which may be sufficiently uniform to produce false calibration curves (zero intersect at some light transmittance value below 100 per cent). To avoid this nitrite absorbing contamination and remove residual azo dyes which may be adsorbed on the coupling flasks and spectrophotometer cuvettes, soak all glassware in 5 per cent aqueous trisodium phosphate for several hours and rinse thoroughly with distilled water. Soak Corex cuvettes only in 37 per cent nitric acid wash, however (31).

The nonabsorption of heavy metal ions on hydrophobic surfaces of PTFE and polyethylene (PE) may be reversed by the presence of certain organic anions. In trace quantities, cesium is adsorbed on glass surfaces by interaction with the layer of adsorbed hydroxyl ions which account for the hydrophilic character of glass surfaces. Addition of a salt of high ionic activity such as sodium nitrate reduces this adsorption effect. The ion exchange capacity of the glass surface can also become a significant factor at very low concentrations. The overall effect is orders of magnitude less (adsorption coefficient increase in the order PTFE-PE-glass) for the non-ionic hydrophobic plastic surfaces. However, the absorption coefficients reverse when the tetraphenyl borate (TPB) ion

is introduced. This reversal is due to adsorption of TPB ions by van der Waals forces on the hydrophobic PTFE and PE which then requester cesium ions. On the hydrophilic glass surface the adsorption is ionic in character which reduces the binding sites for the cesium ions (32).

Lubricants in stopcocks and ground glass joints must be avoided as these materials are a source of contamination and/or absorb those constituents of interest either directly from the air sample or from the liquid reagent system after collection. Teflon[®] plug cocks for stopcocks and sleeves for joints provide seals which require no lubrication or liquid phase sealant for air-tight joints.

Fungus growth within an atmospheric analyzer can be a particularly vexing problem. Fungus within an SO₂ analyzer results in an indicated concentration lower than that actually present. Fungus effect can be minimized in an analyzer by: (a) Keeping the instrument running continually, (b) cleaning periodically, and (c) using a small amount of fungicide in the reagent. Permeation tubes can be inserted into the sample input to test for a fungus problem.

1.3 Solid Adsorbant Collecting Systems—Extended surface adsorbants such as activated silica gels, alumina gels, charcoals and carbons, glass beads, and spheres offer a very attractive solution to the collection and concentration of gas phase pollutants from atmospheric samples. However, the tenacity of the forces which provide quantitative extraction of the components sought may prove to be self-defeating when quantitative removal of these same components for analysis is attempted. Failure to recognize and equate these factors may, and has, produced serious errors. Mercury, either as metallic vapor or as volatile organic derivatives, is not removed quantitatively either by heating or elution with

Table 1. Static Calibration Mixture
Benzene Loss by Absorption on Container Walls
Borosilicate Glass Temperature 75 ± 5 F

Time Elapsed Hours	Benzene PPM		Per cent Loss	Container Conditioned		Remarks Inside Surface Approx. 800 Sq. In.
	Added	Found		Time Hours	Benzene PPM	
0.5	100	56	44	0	none	
0.5	100	67	33	0	none	
16	200	100	50	0	none	
0.5	100	84	16	16	100	
1	..	78	25	
0.5	100	87	13	16	200	
0.5	100	107	-7	Swept, 2nd 100 ppm added
0.5	200	128	36	3rd 100 ppm added
0.5	50	56	-12	Swept, 50 ppm added
0.1	100	75	25	0	none	Idle 30 days
0.25	..	72	28	
0.5	..	55	45	
1.0	..	55	45	
4.5	..	48	52	
24	..	42	58	
192	..	0	100	

Note: Five gallon borosilicate glass carboy jacketed with a canvas cover. Calculated quantity of benzene was added and mixed by rotating a poly TFE paddle and sampled at the indicated time after addition. In two cases indicated by 16 hr (column 5), equilibrated by standing overnight, then refilled.

liquid reagents from silica gel. The same deficiency has been encountered in attempts to use activated charcoal for collection of alkyl lead compounds.

Since the polarity of the adsorbed element or compound determines the binding strength on silica and alumina gels, components of high polarity will displace components of lesser polarity—the principle of chromatography. Therefore, in attempting to collect relatively nonpolar compounds such as benzene, the presence of coexisting polar compounds such as phenol, acetic acid, ammonium chloride must be recognized as a source of interference in the use of solid adsorbants for sample collection. Under high humidity conditions the adsorbant may be deactivated by saturation with water vapor (28). Activated charcoal exhibits this effect only to a minor degree. Aromatic hydrocarbons

are not removed quantitatively from charcoal (36).

Selective displacement may be taken advantage of in eluting the sample from the adsorbant. An inert carrier gas with or without heat, for example, may be used to separate a mixture of aromatic hydrocarbons from a silica gel column. Proper choice of eluting solvent may well serve to separate components by liquid extraction also. An example would be separation of nitrobenzene from aromatic hydrocarbons for analysis by UV spectrophotometry (28).

Liquid elutriants must be chosen and used with care however as decrepitation of the gel may occur. The finely dispersed fragments can produce difficulties in the determination of optical density in the final step of the analysis. This problem is especially acute in UV spectroscopy. Usually this effect is

caused by the heat generated when a polar solvent such as ethanol is introduced. Dilution with a nonpolar solvent such as isooctane will usually avoid this difficulty (28). Elution from charcoal is dependent on molecular size rather than polarity (CS_2 , CCl_4 , etc.)

Change in air flow resistance due to either swelling, shrinking or channeling of the adsorbant is sometimes encountered. Collection of alkyl lead vapor in crystals of iodine was plagued with channeling and shrinkage due to iodine sublimation. Addition of a bed of fine inert sea sand eliminated the problem by providing enough pressure to keep the iodine crystals compacted without appreciably altering the pressure drop across the column (33).

Many dusts are highly adsorbant and often carry a significant gaseous component present in trace amounts such as SO_2 at concentrations below 0.5 ppm. If a prefilter is installed in the collection of trace contaminants, the particulate collected on the filter must be analyzed also if a quantitative accounting for the total contaminant present is desired (34). In some cases such as in the analysis for lead in air, the filter would be analyzed separately from the fraction collection in the liquid reagent to provide a differential analysis for organic and inorganic lead. This is especially important in cases where the TLV's for the two forms are different and coefficients must be used for hazard evaluation (1).

The use of pretreatment or guard systems such as solid dehydrating agents to remove moisture, soda lime to remove CO_2 , or sulfuric acid on silica gel to remove NH_3 interference, and liquid scrubbers as an oxidizing solution to remove reducing interferences such as SO_2 and H_2S before adsorption of the desired pollutant can introduce serious errors (28, 39). Silica based and anhydrous CaSO_4 granules may partially or completely adsorb the subject element or

compound as well as eliminate the interference in the air sample. Careful calibration of the collection system under use conditions is critical when interferences must be eliminated from the air sample by pretreatment before collection of the desired component occurs.

1.4 Diffusion Effects of Plastics—Diffusion outward from the air sample, into, or through plastic containers or tubing probably is one of the most frequent sources of error encountered in air analysis. These irreversible losses are in addition to the reversible surface adsorption effects noted under Section 1.2. Elastomeric materials which include natural rubber, neoprene and plasticized polyvinyl chloride (PVC) are especially troublesome. (see section 3.1 on Permeation Tubes-Dynamic Calibration).

The plasticizers employed in the manufacture of flexible tubing from PVC type polymers may act as cosolvents to remove organic components from air samples by absorption. This mechanism is often temperature sensitive and to some extent may be reversible in a fashion resembling gas chromatography column packings. In a study of the recovery of aniline vapor from air, losses as high as 1.7 per cent/cm of exposed gum rubber tubing were encountered (21). Similar experience has been obtained with alkyl lead and mercury compounds, aromatic hydrocarbons (benzene, toluene, etc.), chlorinated hydrocarbons, and aromatic nitro compounds. An all-glass system with joints and connections fitted with PTFE gaskets and the shortest possible path between air sample intake and the collecting medium to a great extent eliminate these losses. However, adsorption effects must not be neglected even in all-glass systems.

The permeability of even the inert plastics exemplified by PTFE has been employed for the constant rate generation of calibration mixtures of certain trace components such as SO_2 , HF, COCl_2 , aromatic hydrocarbons, etc.

Although this property would be undesirable in the collection of air samples, the magnitude of loss by diffusion through short inert plastic sampling lines (PTFE, polyethylene, polypropylene) can be neglected. However, when samples are stored in plastic bottles or bags, diffusion may become a controlling factor. If plastic containers must be used to facilitate collection or transportation, then the diffusion rate factor must be determined for each component sought over the concentration and temperature range to be encountered and a correction factor applied to correct for the time interval between collection and analysis. Aluminum foil-lined polyester bags (Mylar®) which materially reduce diffusion losses are available for CO₂, CO, water vapor and some other gases but are not recommended for the highly polar gases (SO₂, NO₂ and O₃ (42)). Polyester film in 2-mil thickness is considered the best all-around material for sample-bag fabrication. However, PVC (Saran®) film (1-mil thickness) which has been pre-aged to reduce outgasing of compounds from the plastic into the contents of the bag has been widely accepted on the basis of inertness to many common gases and vapors, high tensile strength and heat sealability. Data relative to air transmission is summarized in the following table (40).

Gas Transmission: ccs/M²/μ/24 hrs./atm at 23 C

O ₂	32-43
CO ₂	150-236
N ₂	4.8-6.3
Air	8.3-17.3

Water Vapor Transmission: gms/M³/24 hr.

at 24 C	0.31
at 38 C	3.05

For ultimate chemical inertness fluoroplastic film bags are available (41).

Laminated plastics—polyethylene on polyester, polyethylene on cellulose acetate and polypropylene on either base—used in packaging foods offer interesting alternatives for gas impervious containers and a choice of surface for contact with the air sample. Semi-flexible 10-liter polyethylene bottles with greater wall thickness also offer a solution to the diffusion problem and are convenient for preparation of calibration mixtures. (See Static Calibration section 2.1).

Inward diffusion also may be encountered and may create problems in shipment or in prolonged storage. Samples taken in a low humidity environment may be altered by inward diffusion of water vapor when the plastic container is stored in a high humidity climate. Solvent vapors, gasoline vapors, gasoline and jet engine exhaust components may contaminate the sample in shipment and show up as unexplained peaks in gas chromatograph analysis or introduce interferences in wet chemical procedures. Shipment in air-tight containers would be a reasonable precaution to avoid contamination from this source.

Although obvious, the testing of all plastic containers, especially thin film bags for gross leaks before use must be emphasized. The absence of pin holes, gaps in the seams, and leakage around the sampling port and in the retaining valve or septum assembly must be verified before each use. This examination may consist of full inflation under slight positive pressure (2-3" water seal) under water or in rigid sealed container with the air line introduced through a bulkhead fitting and connected to a water manometer. Soap solution stabilized with glycerine may be painted or sprayed on for leak detection to pinpoint "micro" leaks.

1.5 Mechanical Defects of Sampling Equipment—As well recognized as this source of error has become, leaks and faulty seals remain one of the major contributors to unreliable results. Any

system used to collect air samples, to remove contamination components by absorption, or to calibrate such systems, must be checked for leakage, either inward or outward depending upon whether the air stream is pushed or pulled. Perhaps the most expedient procedure involves either an increase or decrease of the pressure in the system within limits of the maximum operational range of the system, by closing off tightly and measuring the rate of loss of either the pressure or vacuum on a water manometer. Pinholes in glass seals—especially ring seals—plastic tubing, and metal tubing, joints which do not seal perfectly or are insufficiently gasketed—"O" rings which may be cracked, loose or hardened—or lack a sealing lubricant, loose glass to rubber or plastic tubing connections, dirt in glass to glass joints, glass plugcocks which do not perfectly mate with the stopcock barrels, poor valve stem packing or insufficient sealing pressure, and poorly sealed threaded fittings provide the most frequent leak sources. Pinholes in stainless steel valves, reducing valve diaphragms and two stage regulators also have contributed their share of difficulties (13).

Fouling of rate meters and total volume meters from particulate matter or corrosion products often is not so obvious and requires eternal vigilance to minimize. Orifice type and positive displacement meters and rotameters should be protected by an efficient filter to prevent reduction in orifice opening, erosion of moving parts, or complete pluggage. Rotameter calibration can be shifted significantly by dust accumulation and plastic tube models require protection from solvents which soften or render the bore tacky. Metal floats are attacked by corrosive gases and some reagents such as iodine may in time render the tube body opaque. Corrosive gases and aerosols must be rigidly excluded from total volume and positive

displacement meters to maintain calibration validity and integrity of moving vanes or pistons. Liquid aerosols may be especially troublesome by forming a liquid film which by surface tension and capillary effects reduce air flow in small orifice throats, interfere with the movement of rotameter floats, and increase the resistance to movement of critical components in positive displacement meters. Galvanic corrosion from airborne electrolytes under high humidity conditions can be a problem with metal components.

Flow meters based on thermal conductivity (hot filament type) also are affected by dust and reactive gases, but in a different fashion. Corrosion will alter the electrical conductivity and leads ultimately to failure of the element, and coating by inert material will reduce heat transfer and ultimately reduce the response of the instrument. Chlorides and lead are especially destructive. The volumetric meter and the pump or aspirator sub-assembly of any air sampling system should be adequately protected by appropriate traps which are renewed frequently. Activated charcoal granules (5–10 mesh) probably offer the most efficient protection for all but a few destructive gases and vapors. Cellulose acetate membrane filters (0.8 μ pore size) will effectively remove over 99 per cent of the dust particles which might affect instrument performance without introducing prohibitive pressure drop (43).

The orifice in impinger-type collecting devices, and the interstices in porous glass diffusers are also vulnerable to partial or complete closure by particulate matter and should be protected by a filter when absorbing gases if the solid fraction is not an integral part of the sample. Porous glass diffusers may accumulate particles that are not removed by conventional cleaning procedures after repeated use (13). Also irreversible retention of analyte and sometimes oc-

curs. In the collection of alkyl lead vapors from 5–10 per cent of known quantities added to calibration mixtures were retained in a pencil-type diffuser substituted for the impinger tube in the standard midjet impinger sampler (33). The increase in pressure drop produced by the decrease in free cross-sectional area will contribute to volumetric sampling errors, and may significantly reduce the collection efficiency. In dust collection by impingement, this factor becomes critical.

Pressure drop must be taken into account when a sampling system is calibrated volumetrically. Rotameters and orifice type meters should be calibrated with the pressure reducing or elevating components in place or volume correction made to compensate for the deviations from ambient conditions (44). In systems based on filter collection the pressure drop across the system may steadily increase as the filter medium loads up with retained particulates. Under these conditions an averaged correction may be within tolerable limits of volumetric error. Changes in barometric pressure usually introduce only marginal error if ignored. (Deviation of 15 from 760 Torr will introduce a 2 per cent volumetric error).

In the use of cold traps to collect contaminated air components (freeze-out technique) consideration must be given to the possible accumulation of ice crystals in the delivery tube. This possibility can be minimized by introducing the sample through a side arm into the chamber and exhausting through the inner tube, i.e., reverse flow (14).

1.6 Partial Vapor Pressure Effects—

In collection systems which depend exclusively upon solubility of the component sought in a nonreactive solvent rather than retention by chemical reaction to a nonvolatile derivative, the amount absorbable is determined by the partial pressure of absorbate. The ratio of the air sample volume to the volume

of absorbant is a critical factor in collection efficiency and there is a limiting value of the ratio for any system which cannot be exceeded if a given degree of efficiency is to be attained. In the case of acetone in water the limit would be approximately 5 liters of air through 20 ml of water aliquoted between two bubblers (45). In the case of mesityl oxide which has poor solubility in water to begin with, absorption efficiency would be very poor although relative volatility is low. This is especially critical where a low TLV is involved as large volumes of air would be required. The formation of lower boiling binary and ternary mixtures also can limit absorption. Failure to collect benzene vapor in ethanol even when chilled undoubtedly can be attributed to revaporization at the higher vapor pressure ternary alcohol-benzene-water mixture.

In general, the vapor pressure of the volatile analyte should be reduced to the lowest practical limit by refrigeration to promote efficient collection. In many cases a freeze-out trap without solvent in solid carbon dioxide, liquid air, or a mixture of liquid air and ethanol proves to be a more effective procedure (14).

Sampling in the region at or close to the vapor saturation limit can produce serious errors by condensation in sampling lines. This condition is most likely to be encountered when collecting samples of air at temperatures above ambient and may involve condensation of water vapor which in turn will entrain or dissolve a significant portion of the components present in the sample under high humidity conditions.

1.7 Solubility Effects—Limitation may occur in cases where chemical reaction should, but actually does not occur readily. The classical example is the failure for SO_3 to be absorbed in pure water. The collection of aniline vapor in dilute aqueous HCl is not quantitative; therefore, chilled alcohol is the medium

of choice (16). Until the reaction is initiated by a catalyst, fluorine gas will bubble through distilled water without reacting (to produce FO_2 and HF) although once initiated the reaction may be violent. Other examples which can be cited are failure to obtain absorption of alkyl mercury vapor in acid permanganate and the less than quantitative absorption of alkyl mercury and lead compounds in aqueous iodine reagent (25). The assumption that a given contaminant will be collected based on its reactivity with the reagents can be disastrous if calibration of the system under use conditions is omitted.

If the product from the reaction of the analyte with the collecting reagent has a very low solubility product, losses are to be expected unless care is exercised to avoid the saturation region. The precipitate may adsorb to the container walls, orifice tube, diffuser surfaces or fail to react in subsequent color development. If the solid phase is finely dispersed and has a refractive index approximately the same as the liquid system, the losses may not be observed e.g., silica in chloroform.

Conversely, if the collecting train does not include a prefilter, particulate fractions may go into solution and produce false positive results or interferences, e.g., lead dust or fume in the collection of tetra-alkyl lead vapor (34).

1.8 Temperature Effects—The physical effects of heat on the collection system under normal operating conditions is usually ignored without introducing appreciable difficulties. However, at the design and development stages, attention must be given to the upper and lower temperature limits to be anticipated. At low temperatures components of the liquid reagent may crystallize out or the solvent may freeze. Frequently, a change of solvent will solve this problem (aqueous KI_3 versus methanolic iodine reagent, (25, 33). Close attention must be given to possi-

ble formation of ice or reagent crystals in orifices and porous glass diffusion beds when operating near the freezing range.

On the other end of the temperature scale, excessive evaporation may limit the choice of reagents or sampling time may be reduced below practical limits (again alcoholic versus aqueous iodine reagents). Refrigeration usually can be applied in fixed station or mobile systems to alleviate this problem. A portable assembly which derives its sampling suction from the expansion of difluorodichloromethane vapor through an aspirator also provides useful refrigeration by forming the vaporizer coil into a cavity which will receive a midget impinger (14). In some cases a colorimetric system can be adapted to a non-volatile solvent as illustrated by the use of diethyl phthalate as a solvent for the detection of phosgene in trace ranges over extended periods of time—4–6 hr, (46).

As noted in section 1.6 (Partial Vapor Pressure Effects) the temperature coefficient may be quite large and preclude collection by solution in a solvent above a critical temperature, above which no collection will be obtained, and which may be only slightly above room temperature (45). In general, the adsorption capacity of solid adsorbents is decreased exponentially with rising temperature which may limit the thermal operating range. Temperature coefficients should be determined before sampling is attempted (28).

Excessive evaporation at elevated temperature aggravates the scavenging problem for the metering devices and pump downstream from the collecting unit. Larger activated charcoal cartridges and more frequent replacement must be provided. Generation of volatile components of the reagent will create an even greater problem, e.g., HCl from aqueous iodine monochloride solution (1).

A word of caution with respect to liquid air-cooled freeze-out traps—liquid oxygen from the air sample may condense and create an explosion hazard which may not arise until the trap is removed from the cold bath. In other subnormal systems, moisture may be a mixed blessing. Condensation of water vapor often assists with the retention of contaminants, but in the end interferes with the final analysis. Analytical systems which require anhydrous conditions cannot be employed for air analysis unless dehydration can be employed before the sample enters the collecting system without loss of the analyte (e.g., CO by infrared).

Although temperature extremes, sufficient to alter the mechanical performance of collecting systems, are not often encountered, this factor cannot be ignored when arctic or tropical desert conditions are encountered. Batteries for power supplies must be chosen with these conditions in mind. Piston-type pumps may bind or blow-by check valves may become inoperable, volumetric factors will require recalibration, metering valve and plug cock tolerances may shift significantly, elastomeric components lose elasticity beyond tolerable limits (tubing, "O" ring seals, check valves, gaskets, etc.), and diffusion through plastic containers, especially sample collection and storage bags may become excessive.

Instruments which require electrical circuitry or electronic components for generating analytical data will be affected by temperature extremes and must either be provided with thermal insulation or compensated for altered performance. Extrapolation of response obtained in the range of normal ambient temperature is not a reliable substitute for actual testing under use conditions.

1.9 Volumetric Errors—Rate meters of all types require frequent calibration to detect and correct drift or shifts in reference points, (see Section 1.5).

Portable instruments should be checked every 40–50 hr of operation with at least a secondary standard (wet or dry test meter or glass rotameter) which in turn is compared frequently with a primary standard of the positive displacement total volume type (spirometer).

In volumetric calibration procedures, the pressure drop across the instrument being calibrated and across the system in which it will operate must be determined and appropriate corrections applied (see Section 1.5 for effects of fouling). When filter systems are used, the increasing pressure drop and decreasing sampling rate which develop as the filter loads must also receive consideration. Unnecessary restrictions to free sample flow also produce undesirable pressure drop increments which may limit the range of the sampling system.

Temperature effects do alter volumetric calibration significantly if the system is operated under ambient conditions more than $\pm 20^\circ\text{C}$ from the original calibration temperature conditions. A high degree of volumetric accuracy requires determination of the instrumental temperature coefficient as well as correction of the sample volume to standard temperature and pressure (25°C and 760 Torr.).

Variability in certain types of pumping systems, both between units of the same model or within any given unit, may prevent constant rate sampling within tolerable limits over extended time intervals. Direct current motors are especially vulnerable to rate fluctuations unless effective control circuits are incorporated in the design. Incorporation of a pulse counter which performs as a miniature total volume meter, mechanically or electronically linked to the pump, furnishes a solution to this problem if the rate variations are within limits which do not alter collection efficiency significantly (47). Manually operated squeeze-bulb devices seldom deliver reproducible volumes and should