

SAMPLING

The chemical industry produces material in the gaseous, liquid, and solid states ranging from basic chemicals to functional specialties. In addition, many processes require the use of intermediates which may or not be in the physical form of the products. These various materials are sampled for the purpose of process control (qv), product quality control (see Quality assurance), environmental control, and occupational health control. Samplings of some of these materials can be hazardous, particularly those involving toxic, unstable, or pressurized substances, which require special safety precautions. However, excluding these special circumstances, the main problems encountered in sampling materials in the chemical industry are those of selecting an appropriate sampling procedure and hence sampling device to obtain a representative sample. Experience involving a large variety of materials has produced many methods of sampling, only some of which are discussed herein. Extensive coverage of sampling methods is available from the ASTM (1). A summary of some of the ASTM sampling standards is given in Table 1.

1. Definitions and Problems

Sampling is the operation of removing a portion from a bulk material for analysis in such a way that the portion removed has representative physical and chemical properties of that bulk material. From a statistical point of view, sampling is expected to provide analytical data from which some property of the material may be determined. These data should have known and controlled errors and be produced at low cost.

For pure liquids and gases, sampling is relatively easy. Sampling of these media becomes difficult, however, when particulates are involved. Almost all samples taken in the chemical industry contain solids in some form. Some raw materials, intermediates, or products are themselves particulates; others contain particulates as contaminants. Some materials exist in natural deposits, eg, strata, in a heap on the ground; in storage tanks, bins, pipes, or ducts; in railcars, drums, bottles, and bales; or in other containers that may or may not be subdivided easily into representative units. Furthermore, many systems containing particulates tend to segregate during handling or storage, and this may introduce a sampling error in the form of bias. In a heap of particulate material that exhibits segregation, coarse particles collect at the bottom perimeter of a heap, whereas fine particles concentrate in the center core. For particulate systems that segregate in this manner, the act of pouring the material onto a stationary apex to form a heap, fill a bin, load a conveyor, etc, always results in this type of cross-sectional pattern. Thus, any form of sampling from such a stationary heap is biased with respect to particle size distribution and should be avoided. Because the distribution of chemical components in the material may be size-dependent, even a chemical assay from a sample obtained in this way may be in error.

Generally, little is known in advance concerning the degree of homogeneity of most sampled systems. Uniformity, rarely constant throughout bulk systems, is often nonrandom. During the production of thousands of tons of material, size and shape distribution, surface and bulk composition, density, moisture, etc, can vary. Thus, in any bulk container, the product may be stratified into zones of variable properties. In gas and

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liquid systems, particulates segregate and concentrate in specific locations in the container as the result of sedimentation (qv) or flotation (qv) processes.

Table 1. ASTM Sampling Standards

Material	ASTM standard	Material	ASTM standard
aerospace		graphite electrodes	C783
components	F304	hydrocarbon fluids	D3700
fluids	F301, F302, F303, F306, F309, F310, F329	ion-exchange materials	D2687
		iron ore	E877
		leather and leather products	D2813
aggregates	D75	lime and limestone	C50
sample reduction	F306	magnesium oxide, electrical-grade	D2755
agricultural liming materials	C602		
		metal powders, finished lots	B215
alkylbenzenesulfonates	D1568	metallic coatings, electrodeposited	B602
aluminum and aluminum alloys	E716		
aluminum powder and paste	D480	metallographic specimens	E3
asbestos		metals and alloys, nonferrous	E88, E55
airborne	D4240	metals, for chemical analysis	E173
amphibole	D3879		
cement flat sheets	C459	mica paper	D1677
chrysotile	D2590	microspheres, hollow	D2841
atmospheric analysis		naphthalene, maleic anhydride, phthalic anhydride	D3438
gases and vapors	D1605		
organic compounds	D3686		
bituminous materials	D140	oils, drying; fatty acids and polymerized fatty acids	D1466
bituminous mixtures	D5361		
bituminous paving mixtures	D3665	paints	D3925
		paper	D202
board, electrical insulating	D3394	paper, paperboard, fiberboard, and related products	D585
bleaches containing chlorine	D2022		
brick	C67	particulate matter from stacks and flues, for emission testing	D2928, D3685, D4536
calcium chloride	D345		
carbon black	D1900, D1799	peat materials	D2944
cellulose pulps	D3376	pesticides	F725
cement, hydraulic	C183	petroleum and petroleum products	D270, D1265
cements, thermal insulating	C163		
chemicals, industrial	E300	petroleum products	D4177, D4057
clay tile, structural	C67	petroleum, liquefied	D1265
coal	D388, D410, D2013, D2022, D2234, D4596, D4596	phenol	D3852
		pine oil	D802
		pine tars and pine tar oils	D856
		pinene	D233

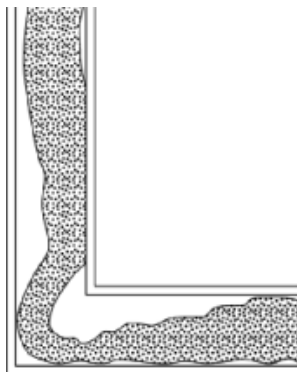


Fig. 1. Particle flow pattern near a 90° bend.

Chemical plants are rarely well designed in terms of sampling capabilities. Thus the rules of sampling are usually not obeyed, and most sampling involves some compromise. Decisions such as the sampling procedure to be employed, the quantity of material to be taken, and the permitted tolerance in the representativeness of the sample must be made on the basis of the use to which the subsequent analysis is to be put. These decisions depend on the analytical facilities available, whether these are manual or automatic, the skill and experience of the sampling personnel, sample and analysis correlation, and cost-benefit relationship. Finally, chemical and physical changes during sampling and subsequent handling need also to be minimized.

Careful consideration of the use to which the subsequent analysis is to be put can save time and effort in the initial sampling and possible resampling operations. For mass loading determination, the collection of particulates from hot ducts may be carried out using filters. If size distribution and classification are necessary to provide data on chemical composition as a function of size, then an in-duct impactor should be used to classify the sample directly at the temperature and location of the sampling nozzle. Agglomeration and aggregation resulting from the formation of liquid and solid bridges upon cooling can transform a flowable particulate into a solid mass which may not be easily redispersed.

Representative sampling demands a knowledge of the chemistry and chemical reactivity of the species being sampled. If a sample is being withdrawn from a hot, high pressure reactor in which the carrier gas is oxygen-free, the extracted sample, when cooled, stored, and analyzed, rarely fails to contact the atmosphere at some stage. This contact can at the least induce hydrolysis and changes in the particulate surface. If size analysis is needed, the atmospheric reaction may not affect the results, depending on the increase of agglomeration or aggregation, but it can significantly affect the surface chemical composition. Physically, the sample may be representative, but chemically it may not be. It is important that steps be taken to minimize possible physical and chemical changes before the sampling operation begins.

The quantity of sample required comprises two parts: the volume and the statistical sample size. The sample volume is selected to permit completion of all required analytical procedures. The sample size is the necessary number of samples taken from a stream to characterize the lot. Sound statistical practices are not always feasible either physically or economically in industry because of cost or accessibility. In most sampling procedures, samples are taken at different levels and locations to form a composite sample. If some prior estimate of the population mean, \bar{x} , and population standard deviation, σ , are known or may be estimated, then the difference between that mean and the mean, \bar{x}_i , in a sample of n items is given by the following:

$$|\bar{x} - \bar{x}_i| = \frac{t\sigma}{n^{1/2}}$$

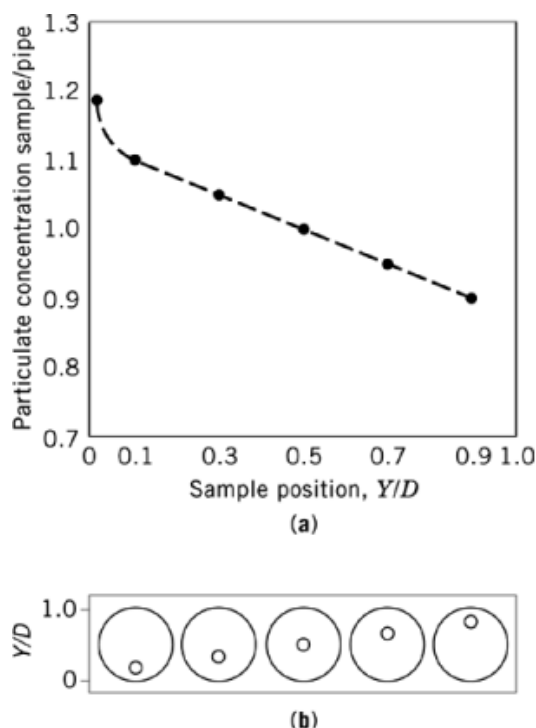


Fig. 2. (a) Particle concentration profile of liquid flowing in a pipe, where Y/D = the ratio of the distance along the diameter to the diameter (\bullet); (b) sampling position, Y .

where t is the test function for differences between mean values. Rearrangement of this equation gives the following:

$$n = \left(\frac{t\sigma}{E} \right)^2$$

where E is the maximum allowable difference between the estimate to be made from the sample and the actual value (4). For example, for a standard deviation of 0.187, the number of samples required to assure with 95 percent confidence that the average quality of a lot lies within ± 0.15 of the mean, the number of samples required is

$$n = \left(\frac{2 \times 0.187}{0.15} \right)^2 = 6.22 (\sim 7) \text{ samples}$$

If the standard deviation of the lot cannot be estimated, a sampling program of greater sample size is required to generate an estimate of the standard deviation for future sampling operations. In some cases, sample size can be increased and sampling costs reduced by the use of automatic samplers. These offer a substantial reduction in labor costs but an increase in capital costs.

The need for skill and experience on the part of sample designers and personnel cannot be overemphasized in chemical plant sampling. Safety precautions are of the utmost importance. Necessary steps must be taken to document the hazards involved in an operation and to ensure that the staff are well-trained, informed, protected, and capable. Except for bulk powder sampling, most chemical plant sampling is hazardous and

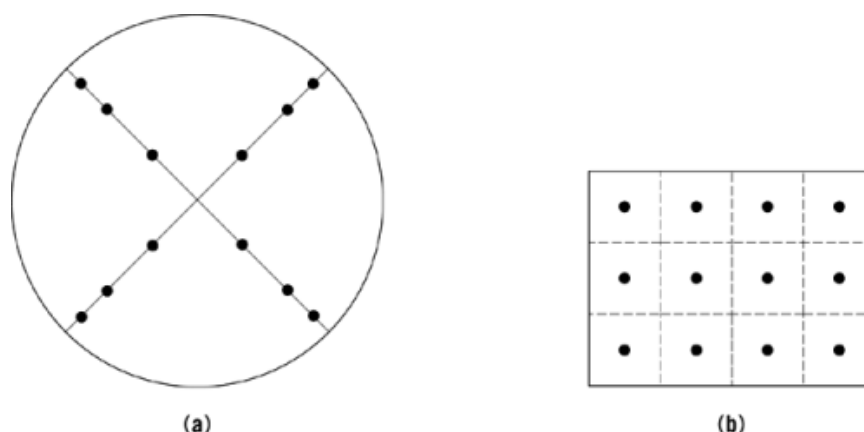


Fig. 3. Location of traverse sampling points. (a) Cross section of stack showing location of traverse points (•) on perpendicular diameters. The circular cross section is divided into three equal areas at $0.5774 r$, $0.8165 r$, and r , where r is the radius. Sampling points are at the centroids of these areas at $0.38 r$, $0.70 r$, and $0.911 r$. (b) Cross section of rectangular stack divided into 12 equal areas having traverse points (•) at the centroid of each area.

difficult and must be designed with care. The following discussions are based on the assumptions that most of these decisions have been made and a satisfactory sampling procedure has been planned.

2. Gases

By far the largest proportion of gas sampling operations in industry is carried out for environmental reasons and the sampling methods employed have been thoroughly researched and are well documented (5–12). The preparation, precautions and equipment requirements involved in the sampling of air pollution sources are applicable to most other gaseous environments (see Air pollution control methods).

Before a source analysis program is undertaken, it is important to decide which information is really required. Sampling sites must be selected with care. Choice of the site can significantly affect accuracy and cost. Care must also be taken in the selection of sampling points at the site. Measurement usually involves the determination of temperature, concentration, and characterization of the gas contaminants. It also requires the mass rates of emission of each contaminant, therefore concentration and volumetric flow data are required.

2.1. Sampling Site

The location of a sampling site and the number of sampling points are based on the need to obtain representative data and whether the points are restricted by access problems. Sampling sites should be at least eight stack or duct diameters downstream and two diameters upstream from any disturbance. A disturbance is interpreted as a bend, expansion, contraction, valve, baffle, or visible flame. Often this type of siting is impossible and compromises have to be made. For rectangular ducts, the cross section should be divided into 12 equal rectangular segments having a sampling point at the centroid of each. For circular ducts, diameter >6.1 m (240 in.) the cross section should be divided into 12 equal areas and sampling points located at the centroid of each annulus on two perpendicular diameters (Fig. 3). For smaller-diameter ducts the number of sampling points can be reduced. If the criteria for eight diameters downstream and two diameters upstream cannot be met, extra sampling points are required (Table 2).

Table 2. Number of Stack Diameters from Flow Disturbance^a

Distance from stack, number of stack diameters		Number of traverse points/dia	Diameter, m
Downstream	Upstream		
>8	>2	8	>6.1
7	1.75	12	
6	1.5	16	
5	1.25	20	
<5	<1.25	24	

^aRef. 13.

2.2. Measurement of Gas Velocity and Temperature

Stack-gas velocity is determined at each traverse point, based on the gas density and a measurement of the average velocity head, using a pitot tube (Fig. 4) (13). The measured velocity pressure is the difference between the total pressure as measured against the gas flow and the static pressure measured perpendicular to the gas flow. The type-S pitot tube has the advantage of easy entry into a duct and a low incidence of plugging when large amounts of particulates are present. However, the tube does not give a direct measurement of velocity pressure, rather it must be calibrated for the velocity being measured. Details of this procedure have been documented by the U.S. EPA (13). Correction factors of 0.78–0.92 have been reported.

During sample and velocity traverses, the S-pitot tube is rarely used in isolation. It is necessary to measure stack or duct temperature profiles to determine variation in gas distribution, and this is usually done at the same time as the velocity profiles. If the temperature measured at each sampling or traverse point are the same, then a single gas sampling point suffices later; but if the temperature varies by more than 5 percent, then the sample point must be withdrawn from the traverse points selected in the initial stack survey. For most purposes, the pitot tube is combined with a thermocouple and sampling nozzle in a sampling assembly. As the presence of other components can significantly affect the correction coefficient applied to the S-type pitot tube, the placement of various components is critical to minimize aerodynamic interference. These placements are shown in Figure 4b and 4c (13).

2.3. Sample Extraction

Once the velocity and temperature profiles have been taken, gas samples can be withdrawn. In the sampling of noncondensable gases which are free of particulates, the gases are extracted from the duct by one of the following methods: a single-point grab sample, a single-point integrated sample, or a multipoint integrated sample. The last method is applicable for the collection of CO₂, CO O₂, excess air, and nitrogen from any process in which other gases and compounds are not present in concentrations likely to affect the result. The sampling probe may be made of stainless steel, borosilicate, quartz glass, aluminum, copper, or Teflon. For a grab sample, a one-way squeeze bulb is attached to the probe to extract the gas. For integrated sampling, the train shown in Figure 5 is recommended (13). A glass or Pyrex wool filter is inserted in the probe tip to remove any unwanted particles, to prevent blockage of the train, and to prevent gas adsorption or reaction on cooling. A pump sucks the gas through a cold trap to remove moisture and then through a rotameter to measure flow rate. The gas is then collected in a gas bag where it is stored prior to analysis. Alternatively, the moisture content is measured directly by passing the gas through a set of impingers in an ice bath inserted in the train (Fig. 6) (13).

Specific trains are recommended for other gases. Sulfur compounds (qv), eg, SO₂, SO₃, H₂S, and mercaptans, are generated during combustion, ore roasting, paper (qv) manufacturing, and other industrial operations (see Sulfur removal and recovery). In most instances, total sulfur is measured. The sampling train for SO₂ is shown in Figure 7 (13). Sulfur dioxide, which is highly reactive, is sampled through a heated or well-insulated

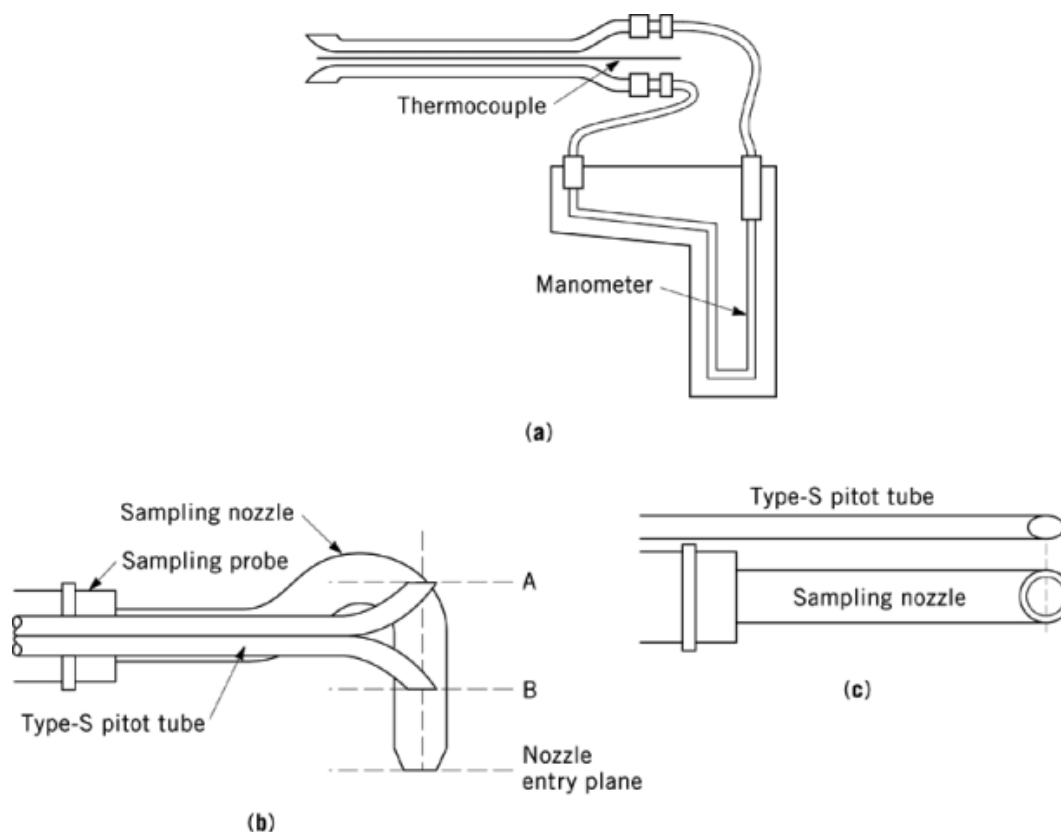


Fig. 4. (a) Type-S pitot tube and thermocouple; (b) side view of the correct pitot tube configuration when used in conjunction with a sampling nozzle, where A is the static pressure opening plane and B is the impact pressure opening plane; and (c) bottom view.

probe and sample line to an impinger train. The probe contains a quartz or Pyrex wool filter to remove particulates. The midjet bubbler in the impinger train contains 80 wt percent isopropyl alcohol to remove SO_3 ; the first two midjet impingers contain 3 wt percent H_2O_2 and the third midjet impinger is dry. The gas is drawn into an silica-gel drying tube. The SO_2 is estimated by titration with 0.01 percent N barium perchlorate using thorin as an indicator.

Nitrogen oxide sampling is simpler. This gas is drawn into an evacuated sample flask containing dilute sulfuric acid and hydrogen peroxide. The flask is shaken and allowed to stand for 16 h before the flask pressure is measured. Then the solution is made alkaline, and the nitrogen oxides are determined by the phenoldisulfonic colorimetric test.

2.4. Sample Extraction When Particulates Are Present

Different designs of probe and train may be required depending on the reason for sampling particulates. The simplest train is for the determination of mass loading only. Representative sampling of particulates is obtained using only isokinetic sampling, ie, when the velocity of the gas in the sample nozzle is the same as the gas velocity in the pipe, duct, or stack. If the sampling velocity in the sample nozzle exceeds that in the duct, the extracted sample is deficient in coarse, because large particles having high inertia do not follow the streamlines

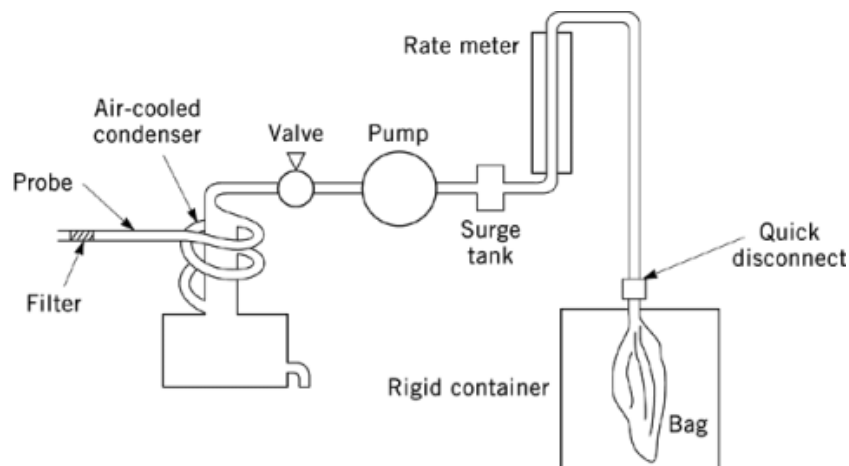


Fig. 5. Integrated gas sampling train.

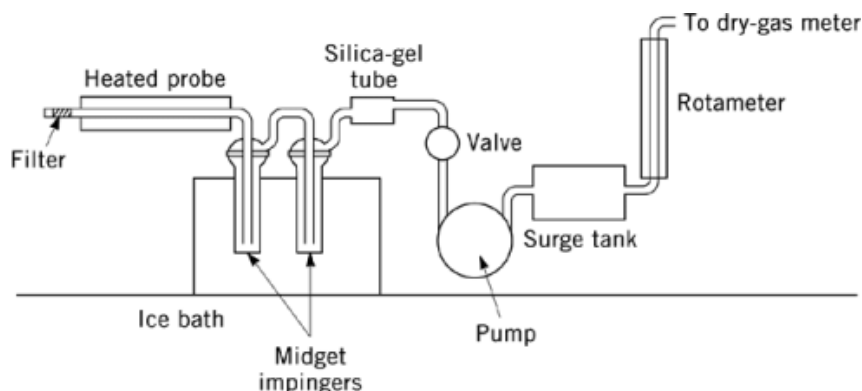


Fig. 6. Moisture sampling train.

and are not collected. If the sampling velocity in the sample nozzle is less than that in the duct, the extracted sample has an excess of coarse, because small particles follow the streamlines around the duct and are not collected. The effect becomes significant for particle diameters in excess of $3\text{--}5\ \mu\text{m}$. Furthermore, the plane of the sample nozzle must be perpendicular to the gas flow or probe misalignment errors become significant.

For mass loadings, particulate matter is withdrawn isokinetically and collected on a glass fiber filter maintained at $120 \pm 4^\circ\text{C}$. The appropriate sampling train is illustrated in Figure 8 (13). The sample nozzle is made of stainless steel having a sharp pointed leading edge. The taper is on the outside to provide a constant internal probe diameter. The probe is usually of a buttonhook or elbow design in order to meet alignment requirements. The first two impingers contain a known amount of water, the third is usually empty, and the last contains silica-gel. Particulate matter, present as solid or liquid at the sampling temperature, is collected on a preweighed filter and determined by weighing. Organic condensable matter is collected in the water, extracted with chloroform and then ether, and weighed after evaporation to dryness. The water is also evaporated to dryness and the residue reported as inorganic condensable matter. Particulates are sometimes present in liquid rather than solid form, eg, as acid mists (14). An alternative system is available for high volume sampling (15).

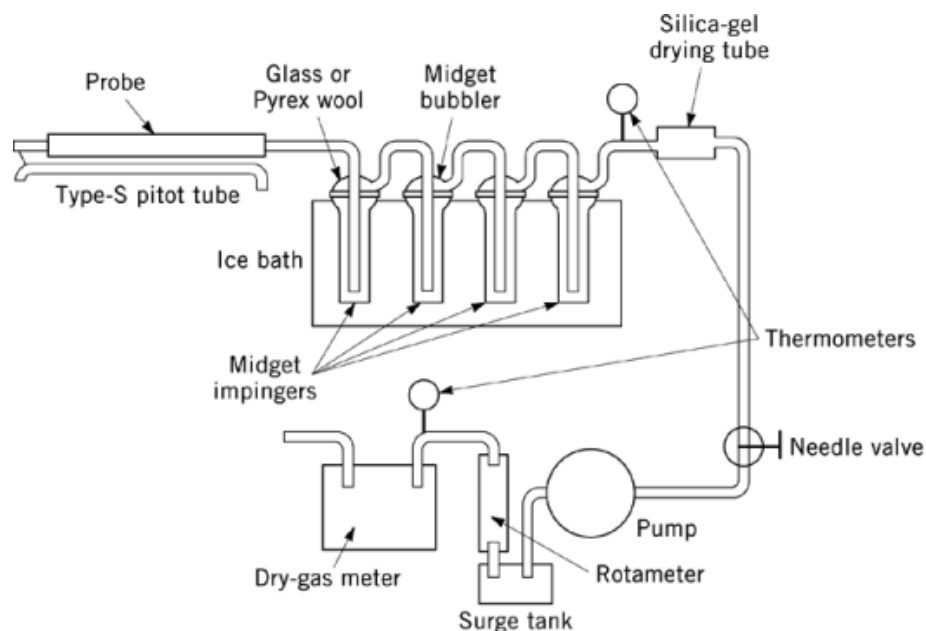


Fig. 7. SO₂ sampling train.

Figure 9 shows the sampling train for sulfuric acid mist collection (13). The first impinger contains 80 wt percent; isopropyl alcohol and the second and third contain 3 wt percent; H₂O₂. The first impinger and filter retain the acid mist and SO₃; the next two retain the SO₂. After sampling, the filter is added to the contents of the first impinger and the total acid is titrated and reported as sulfuric acid.

In many cases, mass loadings are not sufficient. For example, size distributions are needed to correlate respirable fractions in health physics and other operations. Under conditions of high temperature followed by condensation, solidification, and cooling, redispersion of filtered particulates into their original size distribution is rarely possible. In such cases, size distributions are measured directly by use of an in-stack impactor. The Anderson stack sampler (16) is a typical example. The conditions that are necessary for mass loading measurements, ie, isokinetic sampling and nozzle alignment, are required in the use of this type of sampler. The sampler classifies the particulates drawn into the housing according to aerodynamic diameter and deposits different sizes on different collection plates. These can be weighed or chemically analyzed to permit calculation of aerodynamic diameter size distributions and determination of chemical composition as a function of size.

For acid mists, the Brink impactor is often used (Fig. 10) (17). The mist is first drawn through a cyclone to remove particles larger than 3 μm . A five-stage impactor is used to classify mist particles of diameter 0.3–3.0 μm .

3. Liquids

In the chemical industry, liquids are sampled from process vessels, tanks, tanker trucks, tank cars, ships, barges, pipelines, transfer lines, drums, carboys, cans, bottles, open lagoons, settling ponds, sewers, and open flowing streams and rivers. For simplicity, the procedures for sampling liquids are divided into three categories: tanks and similar containers, pipelines (qv), and open streams and lagoons. The problems that arise in sampling liquids containing particulates are not as critical as those that arise in gaseous systems. There are two reasons.

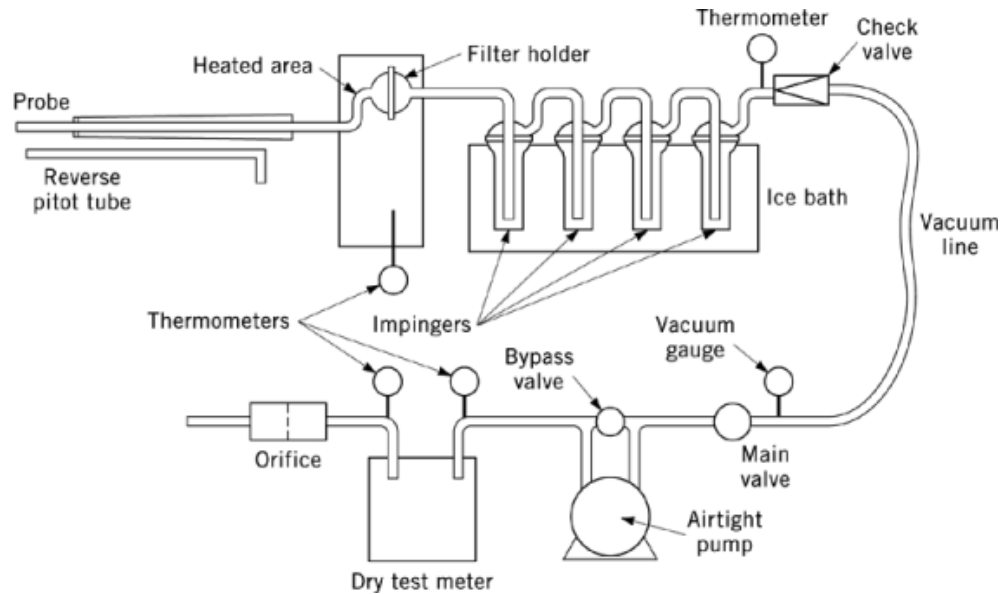


Fig. 8. Particulate sampling train.

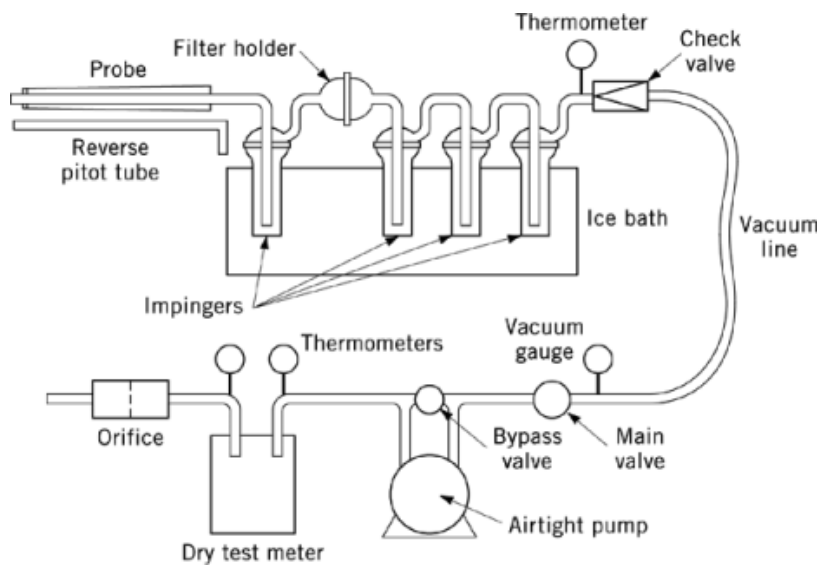


Fig. 9. Sulfuric acid mist sampling train.

Viscosity tends to dampen the effects of sudden changes in flow direction, and particles do not separate as readily from streamlines unless the particle masses and velocities are large.

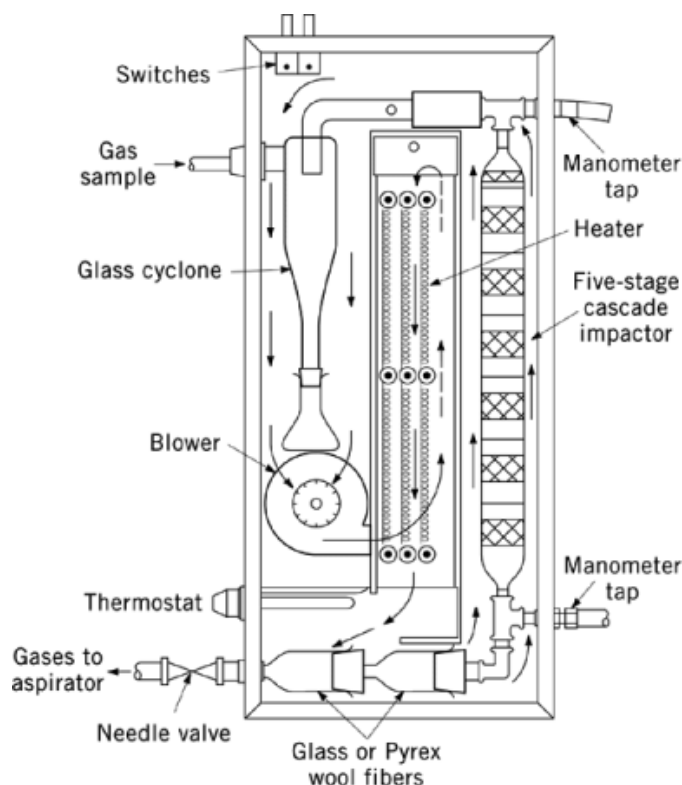


Fig. 10. Diagram of the Brink impactor.

3.1. Tanks

Sampling methods for tanks, trucks, tank cars, barges, etc, usually involve the use of fixed sample taps, thief samplers, or bottle samplers. Tanks are often equipped with stationary taps attached to pipes extending 0.6–0.9 m inside the tank. Usually three taps, one located in each third of the tank height, are sufficient. A delivery tube, long enough to reach the bottom of the sample container to allow submerged filling, is attached to the tap. Separate samples are taken from each tap, or a composite sample is taken by attaching the delivery tube to each tap in succession and filling the bottle one-third each time. When particulates are present, as in slurries or suspensions, representative samples can only be obtained from agitated tanks (see Tanks and pressure vessels).

A more flexible sampling system involves the use of thief tubes and bottle devices. If the tank is designed so that at least half of the cross-sectional area of the liquid surface can be exposed for sampling, samples are withdrawn in a regular grid pattern similar to that used in gas sampling. For thief sampling, the tank is divided into 12 equal areas, and the thief sampler inserted at the centroid of each area. Sample thief tubes for liquids consist of long tubes containing one or more compartments along their lengths which are isolated from the liquid by valves. At a specified depth for single-compartment tubes and upon contact with the tank bottom for multicompartments tubes, the valves are opened and the compartments filled. The valves are closed before the thief is removed from the liquid. Each compartment is analyzed independently or several compartments may be combined to give a composite sample. The bottle sampler is a heavy-metal, perforated screen cage surrounding a one liter bottle, which can be lowered into the liquid. The metal casing weights the bottle so that

it sinks. The bottle is stoppered and, after insertion, the stopper is removed by pulling on an attached line. Separate samples are taken by filling the bottle completely at different depths. In some instances, the sampler is mounted on a rigid rod fitted with a mechanical bottle opener, which allows partial filling to be carried out at a range of depths so that a composite sample may be obtained.

In many cases, access is limited to a single fixed filling hole or vent and only one port is available for thief sampling. This limits the statistical accuracy of the sample and may even give inaccurate information. The sampling thief for drums, carboys, bottles, and cans consists of a hollow tube. This is inserted to a measured depth into the container and the open end closed using a finger or thumb. The tube is removed and the withdrawn sample deposited in a container. Aspirator bulbs or peristaltic pumps are sometimes used to remove larger samples.

3.2. Pipes and Pipelines

Samples may be withdrawn both from closed pipe cross sections and from the outfall of open pipes. The simplest system for the former consists of an in-pipe sampling probe as shown in Figure 11 (18). In the chemical industry, many pipe samples are taken from organic liquids, which may be toxic, highly reactive, and flammable. The amount of sample taken should be minimized in order to reduce worker exposure and sample disposal problems. Adequate ventilation must be provided because the vapors from many liquids are more dangerous than the liquids. Splash guards are necessary when sampling corrosive and toxic liquids. For these applications in-line samplers are preferred. These trap and isolate a predetermined, precise volume of liquid from the line and deliver it to a closed container. Samplers can be installed on either side of the suction or discharge side of pumps. Typical devices include sampling plugs, multiport valves, and pneumatic samplers (19). The sampling plug is usually inserted in a bypass line as shown in Figure 12. The plug has both sample and vent connections. When open, the liquid pumped through the bypass line passes through the plug and can be returned to the line. When closed, a small constant volume of liquid is trapped in the plug and, on rotation of the tap, is drained into the sample bottle while the tap is simultaneously vented (19). If exposure to air can cause a problem in the process, the valve can be vented with nitrogen and then closed before the liquid in the bypass line is returned to the process. Mainstream sampling is usually performed with a sharp-edged probe facing directly into the flow at some preset point. In pressurized systems, sampling sites can rarely be statistically designed with regard to location and once installed are difficult to relocate. Care has to be taken when discharging plug samplers using pressurized systems in order to prevent the liquid venting through the valve connections (19). Sometimes a safety valve is inserted in the bypass to prevent blockage of the pump discharge.

Larger sample sizes can be obtained using multiport valves (19). During normal operation, the liquid flows through the valves in a bypass line. Often two valves are employed. A sample is extracted by turning both valves simultaneously, first to isolate the sample and then to let it discharge into the sample bottle. This is best achieved by gear-and-linkage devices, which mechanically link the two valves. Failure to do this simultaneously can result in the full line pressure being vented through the sample line (19). Thus this type of sampler presents potential hazards when used for high pressure systems.

Air-electric samplers can be installed directly in the pipe wall. One type of liquid sampler is operated by a solenoid valve that activates an air cylinder. A shaft is moved in and out of the pipe by this cylinder and samples are expelled into a container below the sampler. Sample volumes of from 2–30 mL are possible.

For low pressure pipelines that have ports open to the atmosphere, eg, sewers or closed effluent culverts, samplers are designed to sample through manholes. In a typical system, the liquid is lifted through a suction line into the sampling chamber under vacuum. When filled, the vacuum shuts off, and the sample drains into a sample jar. A secondary float prevents any liquid from reaching the vacuum pump. The suction line then drains by gravity back to the source.

A more permanent installation is provided by a chain-driven sampler, widely used in paper (qv) and steel (qv) mills, manufactured as the E Sampler by QCEC (20). A cup, which is attached to a chain positioned

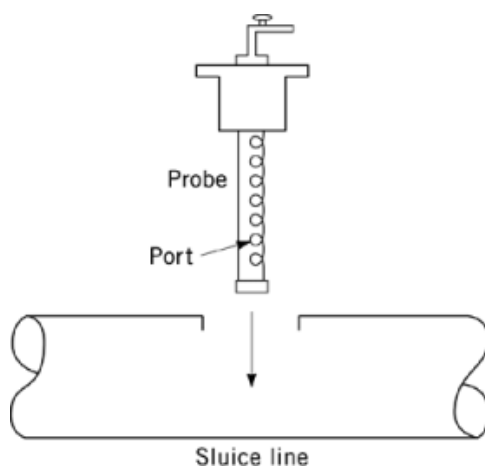


Fig. 11. In-pipe sampling probe having 0.635 cm dia sampling ports.

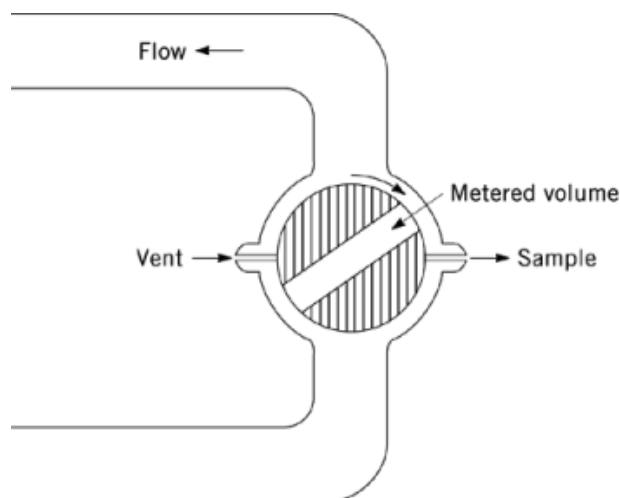


Fig. 12. Metered sampling plug.

perpendicular to flow, travels down through the liquid flow and returns to the upper sprocket, where the sample is drained into a container. Flow-proportional timers can be installed to change the rate of sampling with flow rate (see Flow measurement).

Cutter-type samplers can be installed for low pressure pipelines and enclosed troughs. These samplers contain a movable cutter connected to a flexible hose through which the sample is extracted. Such devices meet all three rules for good sampling: they sample a moving stream, the sample is made up of many increments, and the whole stream is sampled uniformly.

For representative slurry sampling the smallest aperture of the sampler must be greater than three times the diameter of the largest particle present in the slurry. Sample overflow should not occur. The cutter is located in a housing directly in the pipeline and is driven across the whole stream by a motor-driven traverse. Two designs are shown in Figure 13. Cutter samplers can also be placed at the outfalls of pipes or weir discharges (21). Alternatively, a rotary cutter, eg, a Vezin sampler, can be used for flow rates up to 3.8 L/s (18).

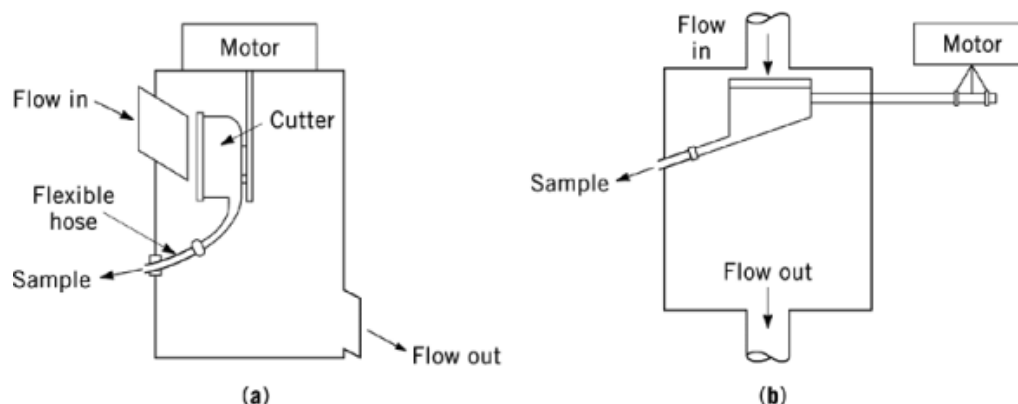


Fig. 13. Slurry samplers: (a) sloping trough cutter and (b) vertical pipe cutter.

3.3. Open Streams and Lagoons

Open-stream discharges are encountered in wastewater plants in the chemical industry (see Wastes, industrial; Water pollution). Settling ponds and lagoons are part of wastewater treatment plants. Details on the monitoring of industrial wastewater are spelled out in EPA regulations (22). Surface samples may be withdrawn using a dipper sampler of nonreactive material (23, 24). Water-pollution abatement programs are based on information obtained by sampling (22). Representative samples are a principal concern of any abatement program. The composition and magnitude of waste flows varies widely. Flow often differs significantly on a cyclical basis. General maintenance is often performed when the plant is not in full production, usually on weekends. This can result in unusually high suspended solids loading in the discharge stream over short periods of time. Boilers may be cleaned at such times and this can give rise to slugs of very highly alkaline water. Lagoon sampling should therefore be carried out every day on a 24-h schedule unless the plant discharge is known to be free of such variations. Several samples should be taken during a 24-h period. The number depends on the variability of the discharge. Ideally the sample should be taken from a place where the flow is well mixed, eg, an oufall from well-mixed tanks, but EPA regulations are often based on the condition of the final oufall to a stream or a river, where the composition can vary widely. Consequently, the flow rate must be measured (22) so that the total waste being discharged can be calculated, and samples must be taken at high frequency in proportion to the flow. Samples are often composited over an 8-h shift or some other suitable time frame.

Many final discharges are mixed effluents. These may contain oil and particulates that tend to separate near the surface or the pipe bottom, respectively. Furthermore, the conditions promoting solids suspension, eg, turbulence, also entrains air into the sample, which can change the dissolved oxygen content significantly affecting chemical oxygen demand (COD) and biochemical oxygen demand (BOD) measurements. Plant-induced turbulence prior to discharge is allowable, but sampler-induced turbulence, eg, vigorously shaking a grab sample prior to pouring it into a sample bottle to suspend the particles, is not good practice. Procedures are also needed to avoid contamination and confusion in labeling. Reference 22 provides detailed instructions for the correct sampling methods.

Preserving the sample is more critical in wastewater sampling than in gas or powder sampling. Biochemical and chemical changes can take place fairly rapidly and thus samples must be analyzed as quickly as possible. For unstable samples, the use of composite samples is not good practice. Instead, special grab samples should be taken and presented to the laboratory for analysis within one hour of sampling. Table 3 gives recommended storage and preservation conditions for various analytical parameters.

Table 3. Recommended Storage Procedures of Samples^a

Analysis	Sample storage	
	Preservation	Maximum holding period, d
total solids	cool to 4°C	7
suspended solids	cool to 4°C	7
volatile suspended solids	cool to 4°C	7
chemical oxygen demand	H ₂ SO ₄ to pH < 2	28
biochemical oxygen demand	lag develops, must use fresh sewage seed	2 ^b
acidity-alkalinity	refrigeration at 4°C	14
biochemical oxygen demand	refrigeration at 4°C	2
calcium	H ₂ SO ₄ to pH < 2	180
chemical oxygen demand	H ₂ SO ₄ , 2 mL/L sample	28
chloride	none	28
color	refrigeration at 4°C	2
cyanide	NaOH to pH > 12, cool to 4°C	14
dissolved oxygen		no holding
fluoride	none	28
hardness	H ₂ SO ₄ to pH < 2	180
metals		
total	HNO ₃ to pH < 2	180
dissolved	filtrate:HNO ₃ to pH < 2	180
nitrogen		
ammonia	H ₂ SO ₄ to pH < 2, cool to 4°C	28
Kjeldahl	cool to 4°C	28
nitrate-nitrite	H ₂ SO ₄ to pH < 2, cool to 4°C	28
oil and grease	H ₂ SO ₄ to pH < 2, cool to 4°C	28
organic carbon	H ₂ SO ₄ to pH < 2, cool to 4°C	28
pH		no holding
phenolics	H ₂ SO ₄ to pH < 2, cool to 4°C	28
phosphorus	H ₂ SO ₄ to pH < 2, cool to 4°C	28
solids	cool to 4°C	7
specific conductance	cool to 4°C	7
sulfate	refrigeration at 4°C	28
sulfide	zinc acetate 2 mL/L sample, NaOH to pH > 9	7
threshold odor	refrigeration at 4°C	7
turbidity	cool to 4°C	2

^aRefs. 25 and 26.^bIn composite sampling system.

Either grab or composite sampling may be used for lagoons. Grab samples are good for continuous flows, but cannot be used for samples proportional to the flow. They are only reliable when the discharge composition is constant. They are essential to pinpoint the times of isolated high pH or high solids content. Composite samples can be taken proportional to flow or time, but such samples provide averages of the conditions of isolated high values of pH and suspended matter to the point where the values of these factors may not be obvious from the final analysis. Another consideration is whether to sample manually or automatically. Manual sampling involves high labor but low capital costs and is necessary when the sampling position is variable. Automatic sampling can involve very high capital costs but is beneficial for high frequency and around-the-clock sampling programs. Automatic sampling can be linked with particle size measurement to give size distributions minute-by-minute. It can also be linked with robot stations for physical and chemical monitoring. Alarms can also be installed to warn of any unusual deviations from normality.

Bacteriological sampling is performed by manual techniques because of stringent sterilization requirements. Samples are taken in wide-mouthed, sterile, glass-stoppered bottles that are wrapped in paper prior to sterilization in an autoclave at 138 kPa (20 psi) or in an oven at 170°C. The bottle is unwrapped and the lower portion is held in the hand. The sample is taken with the bottle mouth in the direction of the flow. The stopper must be protected from contamination, the bottle only partially filled, and the sample stored at 4°C after sampling. For bacteriological samples withdrawn from a tap, the water should run for five minutes and then be shut off; the tap should then be sterilized by flaming before a sample is taken.

Where free chlorine is present, eg, in drinking water, it is measured on-site, and a crystal (eg, 10 mg/40 mL) of sodium thiosulfate is added to the bottle prior to sterilization to convert free chlorine to chloride.

Radioactive samples require other, special techniques. Some are discussed in Reference 22 (see Radioactive tracers).

3.4. Equipment

Manual sampling is performed with one-liter wide-mouthed bottles. A long-handled wide-mouthed scoop is often used for less accessible sampling points. Weighted bottles or specially designed samplers that open at any required depth under water are also used. Hand-operated pumps are used for less accessible sampling locations. A wide range of automatic samplers is commercially available (27, 28). No single sampler is suitable for all sampling needs. Over 40 manufacturers supply automatic sampling equipment and these tend to give widely differing data. The sampling method is more site-dependent than any design attribute (27).

A nonproportional sampler is suitable for near-constant flow conditions. The sample is simply drawn from the waste stream at a constant flow rate. Sampling lines should be as short as possible and free from sharp bends, which can lead to particle deposition. Proportional samplers are designed to collect either definite volumes at irregular time intervals or variable volumes at equal time intervals. Both types depend on flow rate. Examples of some of these are the vacuum and chain-driven wastewater samplers. Other types, which have cups mounted on motor driven wheels, vacuum suction samplers, and peristaltic pump samplers, are also available (26, 27).

Samplers must be designed and constructed to withstand the chemical composition extremes present in the individual discharges. Corrosion-resistant fabrication must be used in the equipment that comes in contact with many chemical industry discharges (see Corrosion and corrosion control).

4. Solids

Solids occur in several forms in the chemical industry. Raw material from natural deposits are compacted in the ground and sampling is performed during the exploration stages. This type of material is typified by minerals and fossil fuels. Before use, these must be crushed, ground into particulate form, mixed, cleaned, and stored. Material may be stored on the ground or in a silo, bin, or hopper. Products in particulate form are usually stored in ships, barges, railcars, drums, boxes, cans, bags, etc. During manufacture these are transported by conveyors, pipes, and chutes and are packaged with the use of free-flowing streams, pneumatic conveyors, spouts, and gravity chutes. Sampling may be required before, during, or immediately after any one of these operations, and different sampling methods are used for most of them (see Conveying).

4.1. Natural Deposits

Natural deposits, eg, minerals and fossil fuels, are located by drilling operations. An auger, eg, a screw or worm, is turned in the earth and pulled out, and material is scraped from the auger for analysis. Alternatively, samples can be taken by hollow core drills which, when withdrawn, enclose a core of the earth that is representative of

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the strata through which the drill has passed. Such core samples are used in geological surveys for fossil fuels. As the drill drives deeper into the strata, each core is extracted and placed in a shallow box and coded so that a complete cross section of the geological strata can be reconstructed. From this, the relative thickness of coal and mineral seams can be directly measured.

4.2. Segregation

Free-flowing powders have a natural tendency to segregate. During transportation, fine particles percolate through coarse ones to give vertical segregation. During pouring, into a heap or into a container, coarse particles travel farther than fine ones leaving, for example, for a centrally poured heap, an excess of fine particles at the center of the heap. Segregation depends therefore on the previous history of the powder. Even nonflowing powders may segregate during manufacture or handling and, once segregated, remain segregated unless subjected to a mixing operation (see Powders, handling).

Whenever possible a powder should be sampled when in motion; and the whole of the stream of powder should be taken for many short increments of time in preference to part of the stream being taken for the whole of the time. Observance of these rules coupled with an understanding of the manner in which segregation takes place leads to the best sampling procedure. Care and skill in abstracting samples is needed and cannot be overemphasized.

4.3. Sampling Stored Material

A very large number of possible systems of stored material exists from which a gross sample has to be extracted. The method to use depends primarily on whether the powder is stationary or moving, and whether it is cohesive or free flowing. It is usual to assume that the powder was mixed before storage. If this assumption is invalid, then the homogeneity of the powder depends on its history. Thus, a nonflowing material that has been segregated prior to storage remains segregated. For a free-flowing material, segregation can occur during transfer from the mixer to the storage container.

4.3.1. *Stored Nonflowing Materials*

Nonflowing materials are composed of very fine cohesive powders, sticky materials, moist material, or fibrous solids. These may be stored in small containers such as drums or bags, or in large containers such as a truck or railcar. In order to obtain a representative sample from a small container, it is preferable that the material be premixed or all the material be passed through a sampling device such as a spinning riffler or Vezin sampler. For large containers, samples may be obtained from the surface or from the body of the material. Surface sampling is usually carried out using a scoop because of simplicity. An assumption is that the powder at the sampling point is representative of the bulk, ie, the powder was mixed before storage. Accuracy is increased by taking more than one sample. Samples should be analyzed separately and combined in later analyses if the variation between samples is at an acceptable level. Body sampling is usually done manually or by a power-driven thief. For the latter, a split-tube thief, ie, a tube having a slot running its entire length, is used with a sharp cutting edge at the lower end of the tube. The thief is inserted in the center of the container and rotated to cut out a core of material. The thief is withdrawn and the material is scraped from it for analysis.

4.3.2. *Stored Free-Flowing Material*

It is practically impossible to representatively sample stationary free-flowing powder because of the severe segregation that has almost certainly occurred. If there is no alternative but to sample this material, several samples should be taken and analyzed separately, so that an estimate can be made of the reliability of the measured parameter. For free-flowing materials stored in small hoppers, drums, cans, boxes, and bags, static sampling by the use of thief samplers is quite common. The typical sampler consists of two tubes, one fitting

snugly inside the other. The tip of the outer tube is sharply pointed, and holes are cut in both tubes to mate at a specific angle of rotation. The outer tube is rotated until the holes are closed, and the thief is inserted firmly into the powder bed. At the desired depth the inner tube is rotated until the holes mate and the thief is opened. Powder flows into the inner tube cavities, after which the tube is again rotated to the closed position. The thief is withdrawn and re-opened to expose the samples. Inner tubes are compartmentalized to ensure that depth profiling can be conducted. Alternatively, a composite sample can be formed.

For larger storage bins, automatic auger samplers are used. A solenoid-controlled air cylinder opens and closes an aperture in the sampling tube, and the sample is drawn to the discharge point by a motor-driven auger. Depth profiles can also be conducted by scoop sampling while the container is being emptied. Sampling thieves have a tendency to arch and thus are vibrated in order to break the arch and allow powder to enter the holes. This is not a recommended practice, however, because fines are more readily admitted. The recommended procedure is to get the powder in motion and obtain a sample using a cutter or Vezin-type sampler.

In the chemical industry it is common to sample small heaps by coning and quartering. The heap is first flattened at the top and then separated into four equal segments with a sharp-edged board or shovel. The segments are drawn apart and frequently two opposite quadrants are recombined and the operation repeated until a small enough sample has been generated. This practice is based on the assumption that the heap is symmetrical. This is rarely so, however, and the withdrawn sample is usually nonrepresentative. This method is no more accurate than the scoop or thief sampling methods, which are simpler to carry out. Coning and quartering should never be used with free-flowing powders, because the most important segregation property is particle size. When poured into a heap, the fines tend to percolate to the center whereas the coarse particles roll down to the outside.

4.4. Flowing Streams

All free-flowing powders are transported at some time during manufacture as flowing streams. Hoppers are emptied by screw conveyors. Solids are transported to bagging operations by pneumatic conveyors, and most solids pass through transfer points in gravity-flow pipes and chutes. Even small samples in boxes, bags, cans, bottles, etc, can be made to flow by emptying them into volumetric feeders. Sampling is carried out on the resultant stream.

Sampling from pneumatic conveyors parallels gas sampling. The exception is that solids loadings can be as high as 50 kg of solids per kg of gas. Commercially available samplers extract particles directly from a transport line. Fixed position samplers are mounted directly on the pneumatic conveyor pipe. Devices are available which extract samples from the product stream by the projection of a sample tube into the flow. Particles impact on the tube and fill the open cavity. The tube is then withdrawn, and an internal screw discharges the collected material (20). In another model, the RX Sampler (manufactured by Gustafson) (29), samples are withdrawn using compressed air.

Sampling from screw or drag conveyors is effected using slide-gate samplers (20, 29). Sampling probes cannot be mounted directly into the lines, therefore sliding gates are positioned on the bottom of drag housing or on the bottom or sides of screw conveyors. An air cylinder opens and closes the discharge gate, permitting powder to fall through the discharge tube into a sample container.

When a sample is to be collected from a conveyor belt, the best position for collecting the increments is where the material falls in a stream from the end of the belt. If access at such a point is not possible the sample must be collected from the belt. The whole of the powder on a short length of the belt should be collected. The particles at the edge of the belt, however, may not be the same as those at the center; particles at the top of the bed may not be the same as those at the bottom. If the belt can be stopped, the sample may be collected by inserting a frame into the stream consisting of two parallel plates shaped to fit the belt. The whole of the material between the plates is then swept out. A scoop can be used to obtain an increment, but this operation can be hazardous if the belt is moving. Bristol Engineering Company (30) manufactures a belt conveyor system

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that has only one moving part in contact with the material. An arm sweeps across the belt to remove the sample.

Sampling from a continuous stream may be continuous or intermittent. In continuous sampling a portion of the flowing stream is split off and frequently further divided subsequently. In intermittent sampling the whole stream is taken for many short increments of time at fixed time intervals. These increments are usually compounded and samples for analysis taken from this gross sample. Consignment sampling is carried out on a single consignment, eg, a truck or wagon load.

For large tonnages, samples taken from conveyors can represent large quantities of material which need to be further reduced. Often, a traversing cutter is used as a primary sampler, and the extracted sample is further cut into a convenient quantity by a secondary sampling device. Secondary traversing-type samplers are marketed by the Denver Equipment Corporation, QCEC, and Gustafson, Inc. This equipment is satisfactory for many applications. Limitations which restrict use, however, include the following: although comparatively easy to design and build in a new plant, it is frequently difficult and expensive to retrofit an existing plant, primarily owing to space requirements; the quantity of sample obtained is proportional to product flow rate and this can be inconvenient when the plant flow rate is subject to wide variations. On the other hand, where a plant's daily average is required, this is a necessary condition; and it is difficult to enclose the sampler to the extent required to prevent the escape of dust and fume when handling a dusty product.

Commercial samplers are available that combine a traversing-type sampler and an unacceptable table sampler. An alternative design is the radial cutter or Vezin sampler. These samplers vary in size from a 15-cm laboratory unit to a 152-cm commercial unit.

4.5. Efficiency

Sampling of bulk solids from grinding circuits or chemical plants represents tons of material per day. A primary sampler generally removes 10–100 kg as a gross sample, which is then subdivided into 1–10 kg laboratory samples by a secondary device. The samples may be examined as taken or may be crushed prior to examination. Measurement samples are needed by the laboratory in gram or milligram quantities and on the basis of subsequent measurement decisions are made as to the quality of tonnages of bulk material. It is therefore essential that the measurement sample be representative of the bulk. Bias at any stage of the sampling affects the final result (31).

In one sampling method study, sugar, coarse sand, and fine sand were used to test several laboratory sampling procedures (32), eg, cone and quartering; scoop sampling, which consists of plunging a scoop into the powder and removing a sample; chute splitting; table sampling; and rotary riffing. The rotary sample divider consists of a hopper and vibratory feeder, from which powder is made to flow in a constant stream. The powder falls onto a rotating circular tray subdivided into various compartments. Several versions of this instrument are available handling from 40 liters down to a few grams.

Scoop sampling is particularly prone to error because the whole of the sample does not pass through the sampling device, and the sample is taken from the surface where it may not be representative of the mass. In an attempt to achieve a good mix the sample container is shaken prior to sampling. In a sampling table the material is fed to the top of an inclined plane in which there is a series of holes. Prisms placed in the path of the stream break the stream into fractions. Some powder falls through the holds and is discarded. The powder remaining on the plane passes on to the next row of holes and prisms. More is removed, and so on. The powder reaching the bottom of the plane is the sample. The chute splitter consists of a V-shaped trough along the bottom of which is a series of chutes alternately feeding two trays placed on either side of the trough. None of these methods gives as efficient a sample as the rotary sample divider. The results of this study are given in Table 4. Rotary sampling is by far the best analytical sampling method to use for solids. This method follows all the rules for good sampling.

Table 4. Reliability of Solids Sampling Methods

Method	Standard deviation, %	Estimated sample error, % ^a
cone and quartering	5.76	19.2
scoop sampling	6.31	21.0
table sampling	2.11	7.0
chute riffing	1.10	3.7
rotary riffing	0.27	0.9
random variation	0.09	0.3

^aValues are maximum.

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