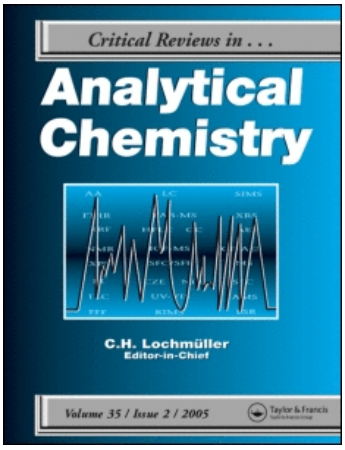

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Denudation — A Convenient Method of Isolation and Enrichment of Analytes

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ABSTRACT: A wide variety of analytical techniques can be applied for the determination of trace components of air. Usually, a direct determination of analytes in an air sample is impossible, and a need arises to employ suitable techniques of their isolation and preconcentration, prior to the final determination stage. Any of these techniques may be included into one of the following, basic groups:

- dynamic techniques
- passive techniques
- denudation techniques.

For several years, a rapid growth of interest in the denudation techniques has been observed, although their theoretical principles had been known long before, because they facilitate the studies in the physical speciation analytics.

The objective of this paper is

- presentation of the theoretical principles of denudation techniques,
- discussion of the major practical constructions of denuders,
- reviewing current range of applications of these techniques.

KEY WORDS: denudation, denuders, analyte enrichment, physical speciation, trace pollutants, air protection.

I. INTRODUCTION

A trend toward possibly the most accurate knowledge of the state of environment and undergoing processes has become a moving force for the development of environmental analytics and monitoring. There are several reasons for the continuous improvement in methods and techniques of monitoring environmental pollutants. Due to rapid progress in science and medicine, our knowledge of the effects brought about by the presence of a wide variety of chemical compounds in the environment steadily increases. The mechanisms of interactions between these compounds and other constituents of the environment are increasingly better understood. The majority of the compounds in question are of anthropogenic origin — their presence in the environment

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results from the rapid industrial developments in the 20th century, which brought, for example, SO_2, N_xO_y, pesticides, dioxins, etc. Still, it is only now that the ecological threat caused by their introduction to the environment can be assessed properly.

On the other hand, undertaking suitable steps leading to the elimination or minimalization of the effects of the aforementioned interactions calls for a suitable strategy to be applied. Collecting the data, possibly accurate, on the state of the environment becomes a necessity, implying the development of appropriate techniques of measuring the degree of contamination of waters, soils, and air.

As the atmosphere constitutes the element of the environment that humans come most frequently in contact with, the assessment of its quality becomes the main factor in assessing the resulting risks for human organism. Heterogeneity of the system (i.e., the atmosphere) plays an important role here. Numerous factors influencing environmental toxicity of any given compound depend not only on its amount but also on its presence in a given phase. The latter may influence the form of a compound (e.g., NH_3, NH_4^+), as well as the extent and rate of its absorption by plants and animals.[1] Interphase distribution also influences the ways of propagation of pollutants in the atmosphere (also indirectly, e.g., by influencing the compound's ability to enter into secondary reactions).[2,3]

Air pollution monitoring covers both outdoor and indoor air. The latter type of monitoring includes studies on the so-called sick building syndrome (SBS),[4] aimed at the determination of volatile organic compounds (VOCs) in closed rooms. Another important effect of the air pollution is damage done to historic buildings and monuments. Such damage is related to the deposition and/or binding on the surfaces exposed of compounds such as sulfur dioxide, nitrogen oxides, hydrocarbons, and other particles of dissolved or dispersed matter.[5]

Beyond any doubt, one can conclude that the trend toward the determination of a possibly wide spectrum of analytes (both organic and inorganic), at still lower concentration levels, is becoming the main task in the development of environmental analytics and related instrumentation.[6]

II. ISOLATION AND ENRICHMENT OF ANALYTES

Techniques employed in pollution monitoring should fulfill the following general requirements:[7]

- a sample collected must be representative,
- the sampling procedure should be simple and applicable under any conditions,
- the analytical procedure should be a selective, possibly specific, one,
- results obtained should be reproducible,
- no changes can occur between the sampling and the final determination stage.

A wide variety of sampling techniques, including enrichment of analytes has been elaborated. The general classification of these methods, accounting for the phenomena utilized at the enrichment stage, is shown in Figure 1.[8]

The dynamic methods of enrichment are based on passing of the stream of air through a suitably built container in which certain components of the analyzed air sample are retained (enriched). The complete apparatus for dynamic enrichment of analytes comprises the aforementioned container (trap), an adequate pump with its power source, and devices for measuring the volume and/or the flow rate of the stream of air.[9]

In the case of the passive methods, compounds in question enter the container filled with the retaining medium from its close vicinity by the way of diffusion or permeation. The amount of the component retained

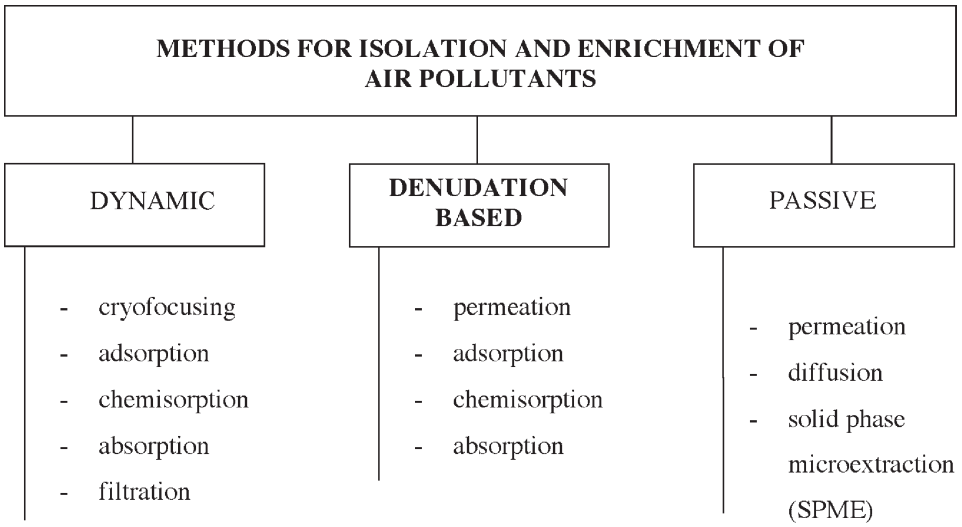

FIGURE 1. The classification of sampling methods, including simultaneous analyte enrichment based on the phenomena utilized for the analyte enrichment.

in the trap is proportional to its mean time weighted concentration in the surrounding air.[10]

In both cases, the analytes of interest are retained in the trap filled with the proper absorbing or adsorbing agent. The principal difference lies in the forced flow of the sample through the trap in the dynamic techniques.

In a context of the aforementioned requirements imposed on analytical methods, the fact that atmosphere, being a complex system, comprised of gases, liquids (aerosoles), and solid particles, leads to significant difficulties. Air, treated as a heterogenous system, requires the employment of special apparatus designs. The difficulties become remarkable, if a method utilizes sorption devices capable of filtering, when the presence of solid particles in the sample matrix can influence, in different manner, the results of determinations of gaseous components of the sample.[11-13] In a case when analytes are present in both phases and the solid phase is being deposited (on a filter or a sorbent bed) during the passage of air through the sampler, this deposited solid phase can cause the sorption of the less volatile or the liberation of the more volatile compounds, hence resulting in changes in composition of the analyzed sample. On the other hand, collecting the analytes from the air without any filters can lead to the simultaneous retention of analytes from all phases and subsequent significant errors, particularly in the analysis of organic compounds.[14]

A way to solve or bypass these problems lies in the utilization of denuders (Figure 2). The phenomenon of denudation involves movement of molecules and/or particles being as a result of two forces:

- a force vectored in accordance with the direction of the gas stream, resulting from the forced flow of gas,
- a force perpendicular to the longitudinal axis of the denuder (and its walls), resulting from the radial diffusion.

Under such conditions, the combined process of isolation and enrichment of analytes can proceed directly from the primary (original) matrix: analytes present in the gaseous phase are retained by the sorption medium, due to their high diffusion coefficients, while solid particles can pass

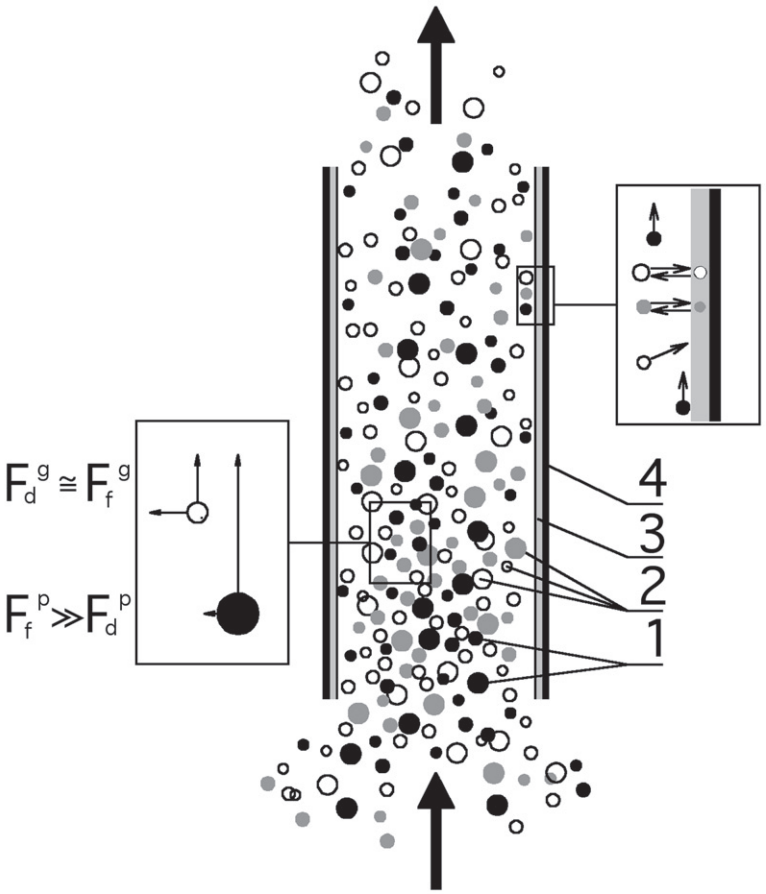

FIGURE 2. The principle of separation of molecules of gases and vapors from solid particles in a cylindrical denuder: 1 — solid particles, 2 — gas molecules, 3 — film of the retaining medium, 4 — walls (F-force; indices: g–gas, p–particulate matter, d–diffusion, f–gas flow).

the tube practically avoiding any contact with the walls of the device. Additionally, solid particles leaving the denuder can be retained on an appropriate filter, thus permitting physical speciation analysis.

Proper operation of a denuder depends on several conditions (asterisks mark conditions specifically related to denuders):[15,16]

- flow of gas must be stable and laminar.*
- analyte releasing technique cannot influence sample composition,
- the device should be operated under steady — state conditions of pressure and temperature,
- temperature and viscosity distributions must be uniform within the stream of gas,*
- longitudinal diffusion of the analyzed gaseous components should be negligible as compared with the linear velocity of gas flow,*
- sorption material should be a good sink for the analytes in question,
- adsorbate should not undergo any secondary transformations within the denuder, that is, neither new compounds should appear, or those already present disappear.

III. THEORY OF DENUDATION PROCESSES

Intensive research on utilization of denudation processes in analytics has been con-

ducted since the early 1970s, that is, since their first practical application.[17,18] Both theoretical and practical aspects of the utilization of the technique have been described.[15,19-21] Theoretical principles governing the operation of several practical constructions of the denuders: cylindrical,[22] annular,[23-26] diffusion scrubbers,[27] or "hanging drop" type[28,29] have been elaborated. These constitute a basis for all other constructions. The last section of this theoretical section is devoted, due to its increasing significance,[30] to the theory of analyte enrichment based on the equilibrium-sorptive-enrichment (ESE) technique.

A. Theory of Cylindrical Denuders

If c_A denotes concentration of component A in air [mol/cm^3], then one can write that $c_A = f(t, x, r)$, where t is time [s], x – longitudinal coordinate [cm], and r – distance from the longitudinal axix of the cylinder [cm].

In a general case, the balance of component A in the denuder (Figure 3) is given by the following differential equation:[22]

$$\frac{\partial c_A}{\partial t} = -\upsilon \frac{\partial c_A}{\partial x} + D_A \frac{\partial^2 c_A}{\partial x^2} + D_A\left(\frac{\partial^2 c_A}{\partial r^2} + \frac{1}{r}\frac{\partial c_A}{\partial r}\right) - r_A \qquad (1)$$

where:
υ — actual linear velocity of air flow [cm/s], for a laminar flow given by equation:

$$\upsilon = 2\upsilon_{av}(1-r^2/R^2);$$

υ_{av} — linear velocity of air flow [cm/s];
R — internal radius of the denuder [cm];
D_A — diffusion coefficient of component A in air [cm^2/s];
r_A — component A gas-phase reaction rate [mol/(cm^3·s)].

Equation 1 describes the rate of change in the concentration of component A in the cylinder, resulting from: the forced movement of the air along the denuder (first term), longitudinal diffusion (second term), radial diffusion third term, and a homogenous chemical reaction (fourth term).

It is obvious that the solution of the equation depends on the assumed initial conditions (t=0) and boundary conditions with respect to x (from x=0 to x=L, where L is the cylinder lenght) and r (from r=0 to r=R). It should be noticed, that the case of r=R should include any heterogenous chemical reaction between component A and the stationary phase material.

Besides the boundary conditions, additional assumptions[22] have to be made to solve Eq. 1. The first, and the most commonly used one, is the assumption that composition of the air does not change during its flow along the denuder, *i.e.*, $\partial c_A/\partial x = 0$. Subsequently, one can omit, with satisfatory approximation, the second term of the equation, $D_A(\partial^2 c_A/\partial tx^2)$, due to the fact that linear velocity of molecules of component A resulting from longitudinal diffusion is negligible compared with linear velocity of the air stream pumped through the denuder $\upsilon(\partial c_A/\partial x)$. Such a situation exists when the Peclet number, $2R\upsilon/D_A$, is greater than 10. The last approximation lies in assuming that no homogenous reactions occur in the denuder (the pollutants neither are formed, nor they disappear), $r_A=0$. Introducing these assumptions permits simplification of Eq. 1 to the form:

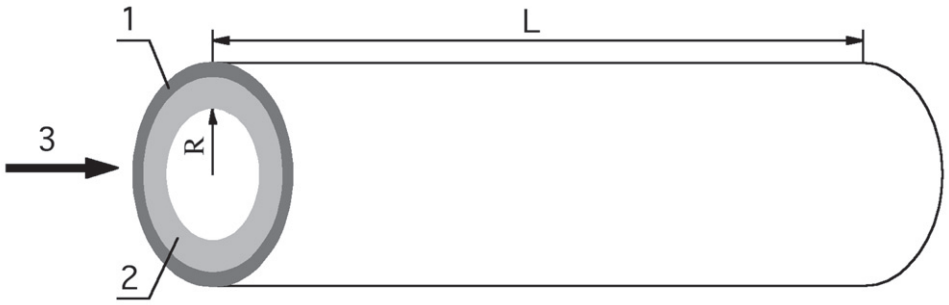

FIGURE 3. A schematic view of a cylindrical denuder: 1 — cylindrical walls, 2 — retaining medium, 3 — air flow, R — radius, L — length.

$$\frac{\partial c_A}{\partial t} = D_A\left(\frac{\partial^2 c_A}{\partial r^2} + \frac{1}{r}\frac{\partial c_A}{\partial r}\right) \qquad (2)$$

Further assumptions, that: component A is present in trace concentrations; the flow is laminar; the temperature is constant; and the amount of retained component A is small, when compared with the capacity of the stationary phase; lead to the best known Gormley-Kennedy (GK) solution:[31,32]

$$\frac{c_{av}}{c_o} = 0.8191\,exp\left(-7.314z^*\right) + 0.0975\,exp\left(-44.61z^*\right) + 0.0325\,exp\left(-113.9z^*\right) + \ldots \qquad (3)$$

where:
c_o — concentration of analyte A in the gas stream at denuder inlet;
c_{av} — average concentration of analyte A in the gas stream leaving the denuder;
z^* — equivalent length (dimensionless) given by equation:

$$z^* = \frac{\pi}{2} \times \frac{D_A L}{V} \qquad (4)$$

where:
L — length of the cylinder [cm];
V — volume air flow rate [cm^3/s] through the denuder, accounting for the actual conditions in the device.

Equation 3 can be further simplified by dropping all the terms on the right side but the first. It is still a fair approximation, leading to an error of *ca.* 1%, when z^* is of the 0.1 order of magnitude.[22] Relations 3 and 4 indicate that the effectiveness of a cylindrical denuder ($1- c_{av}/c_o$) increases with an increase in the length of the denuder and the diffusion coefficient of the compound in question, and with a decrease in the gas flow rate.

B. Theory of Annular Denuders

A denuder of this type is formed by a cylindrical tube with an internal, coaxial, also cylindrical rod (Figure 4). The air is passed through thus formed annular space. Stationary phase (sorption material) is placed on the internal wall of the tube and the surface of the rod.

A relation describing the effectivness of analytes retention in annular denuders was derived for the first time from the Gormley-Kennedy Eq. 3 by Possanzini.[23] To obtain the equation, analogous to that for cylindrical denuders, based on the first term of Eq. 3, one should modify Eq. 4 to the following form:

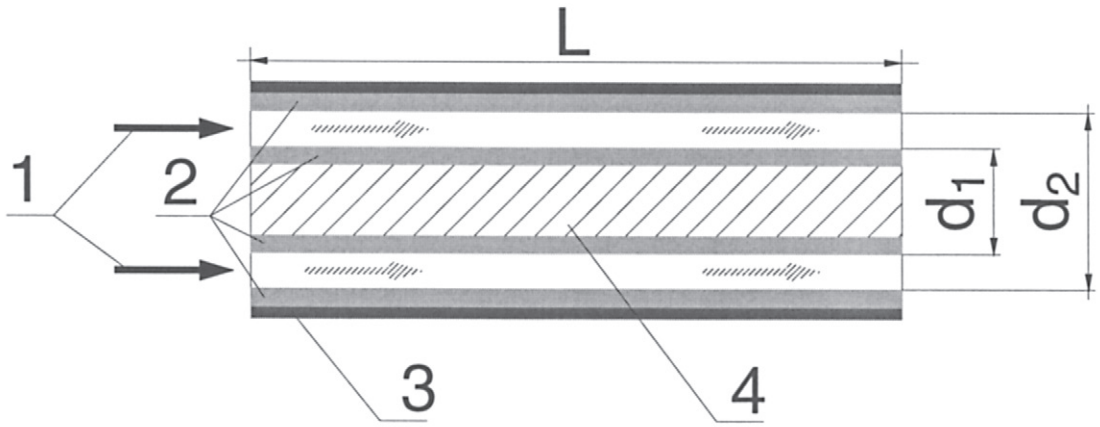

FIGURE 4. A schematic view of an annular denuder: 1 — air flow, 2 — retaining medium, 3 — cylindrical walls, 4 — rod, d_1 — annulus internal diameter, d_2 — annulus external diameter.

$$z_a^* = \frac{\pi D_A L}{2V} \times \frac{d_1 + d_2}{d_2 - d_1} \qquad (5)$$

$$\left[\frac{V}{L}\right]_a = 1.54 \times \frac{d_1 + d_2}{d_2 - d_1} \times \left[\frac{V}{L}\right] \qquad (7)$$

where:
z^*_a — equivalent length for an annular denuder (dimensionless);
d_1,d_2 — smaller and larger diameter of the annular space, respectively.
Therefore, the equation describing the c_{av}/c_o ratio for the annular denuder assumes the following form:

$$\frac{c_{av}}{c_o} = A\,exp\left(-\alpha z_a^*\right) \qquad (6)$$

The two constants, A and α must be determined experimentally. On the basis of Eq. 5, one can conclude that effectivness of annular denuders can be optimized not only by varying denuder length, L, or volume air stream flow rate, V, but also by suitable choice of the ring width. Reducing the width (d_2 - d_1) and increasing d_1 results in much larger values of z^*_a, even at the same V/L ratio, when compared with z^* calculated on the basis of Eq. 4. The comparison of efficiencies of both denuders leads to the following relation:[23]

C. Theory of Analytes Enrichment Analytes Based on the Equilibrium (Ad)sorption Technique

In the case of the equilibrium (ad)sorption technique, the stream of air is pumped through the trap at ambient temperature and constant flow rate. Although, as opposed to the previously described methods based on an adsorption-thermal desorption (ATD) cycle, volume of air passed through a denuder is much larger than the breakthrough volume of the retaining medium.[33] In other words, the breakthrough volume does not constitute a critical parameter of this process. This approach is quite different from that utilized in methods based on the breakthrough volume, where, to increase the effectivness of analytes retention from the stream of air, one uses possibly strong adsorbents.[34] The equilibrium (ad)sorption technique is based on the partition of an analyte between the gas phase and the retaining medium (driving force of this process is the difference in the activity of the analyte in the gas phase and in the sorbent). Therefore, one can utilize enriching media of weak sorp-

tive properties. Among the advantages of such an approach, one should mention there is no need for high temperatures at the thermal desorption stage, also displacement of some analytes by the others can be avoided, permitting the elimination of the influence of air humidity on the analyte isolation process.

Additional advantage lies in the possibility of calculating the enrichment coefficient directly from the chromatographic retention data. One can define it as follows:[35]

$$E_F = \frac{c_{g,T_d}}{c_{g,T_s}} \quad (8)$$

where:
$c_{g,Ts}$ — concentration of an analyte in the gas stream at the trap inlet at temperature T_s;
$c_{g,Td}$ — concentration of an analyte in the gas stream at the trap outlet at temperature T_d.
The two concentrations can be expressed by the following relations:

$$c_{g,T_d} = \frac{c_{s,T_d}}{K_{D,T_d}} = \frac{c_{s,T_d}}{k_{T_d}\beta} \quad (9)$$

$$c_{g,T_s} = \frac{c_{s,T_s}}{K_{D,T_s}} = \frac{c_{s,T_s}}{k_{T_s}\beta} \quad (10)$$

where:
$c_{s,Ts}$, $c_{s,Td}$ — concentration of an analyte in the stationary phase at T_s and T_d;
k_{Ts} , k_{Td} — relative capacity factors of the stationary phase;
$K_{D,Ts}$, $K_{D,Td}$ — partition coefficients of the analyte;
β — volume ratio of the two phases (V_g/V_s) in the denuder.
T_s and T_d denote temperature of sorption and desorption, respectively.

The total amount of an analyte retained in a denuder, m_p, can be expressed as:

$$m_p = c_{g,T_s} \times V_g + c_{s,T_s} \times V_s \quad (11)$$

Where V_g and V_s are volumes of the mobile (gas) and the stationary phase, respectively. An analogous equation describes the total amount of an analyte remaining in a denuder after desorption (heating), where the concentrations at an elevated temperature, T_d, are used:

$$m_p = c_{g,T_d} \times V_g + c_{s,T_d} \times V_s \quad (12)$$

After the substitution of equations 9 and 10 into 11 and 12, dropping the first term at the right side of Eq. 11 ($c_{g,Ts} \times V_g$ is much smaller than the second term. Additionally, this amount is usually lost when the trap is flushed with an inert gas before heating), one can get:

$$c_{g,T_d} = \frac{c_{s,T_s} \times V_s}{V_g \times (k_{T_d} + 1)} = \frac{c_{s,T_s}}{\beta \times (k_{T_d} + 1)} \quad (13)$$

Using Equations 13 and 10 in Eq. 8 leads to the final form of the latter, permitting the calculation of the enrichment coefficient:

$$E_F = \frac{k_{T_s}}{k_{T_d} + 1} \quad (14)$$

Usually, the inequality $k_{Td} << 1$ is true; therefore, one can approximately assume that the enrichment coefficient is equal to the value of the capacity factor of the stationary phase for a given analyte at sorption temperature (T_s). The above equation also indicates that performing measurements of capacity factors at two temperatures permits a simple, experimental determination of the enrichment coefficient.

IV. DESCRIPTION OF POSSIBLE DENUDER DESIGNS

A. General Characteristics

One can mention several trends in the development of the denudation technique as a method of isolation and analyte enrichment prior to the final determination stage:

- seeking new, more effective designs, such as, annular denuders, honeycomb type denuders, or parallel plates type denuders,
- a drive toward lowering the detection limit that resulted in designs of so-called high volume samplers, *e.g.*, BIG BOSS,[36] IOVPS,[37-39]
- increasing the specificity of the analyte retention stage,[40-42]
- automatization of the process, leading towards development of so called wet denuders and thermodenuders.[43-45]

Generally, the above listed factors are common for all analytical techniques; nevertheless, the denudation offers an additional advantage, that is, an opportunity of "physical speciation".[46-49] This is reflected both in instrument design and the procedures applied. In the design, the main task is to avoid and/or prevent any contact of solid particles with the adsorbant surface. Ii is most frequently achieved by adding cyclones (with inner walls coated with inert materials, *e.g.*, PTFE) at the denuder inlet to remove particles larger than 2 μm. The same effect may be ensured using special, highly efficient impactors.[50,51] A schematic configuration of an instrumental setup for analyte isolation from a stream of air using denuders is shown in Figure 5.

In the case of the procedures, one can distinguish two approaches. The first and simplest one is based on the utilization of comparative analysis. In these methods, determination of sample composition is not performed directly but through a comparison of results obtained by traditional methods (gas and solid phase analysed as a whole) with those obtained by diffusion based methods (gas phase only).[52-54] The other approach is based on utilizing extractable stationary phases in a parallel system, called by the authors an integrated organic vapor/particle sampler (IOVPS).[37-39]

Considering analytical procedures, one should mention another aspect of denuders utilization, namely, an opportunity of using suitable set ups, permitting the simultaneous determination of compounds of different chemical properties. Such an operation can be performed by placing several denuders, with different retaining media, either in parallel or in series. Necessity for the utilization of different media for retention of analytes is particularly important in analyses of inorganic compounds (*e.g.*, mixtures of basic and acidic compounds), and also results from limitations of the detectors used.

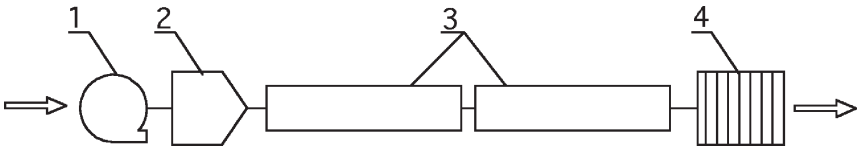

FIGURE 5. Complete, denuder-based device used for sampling analytes from an air stream: 1 — cyclone (PTFE), 2 — impactor, 3 — denuder (or several denuders, here connected in series), 4 — filter (or set of filters).

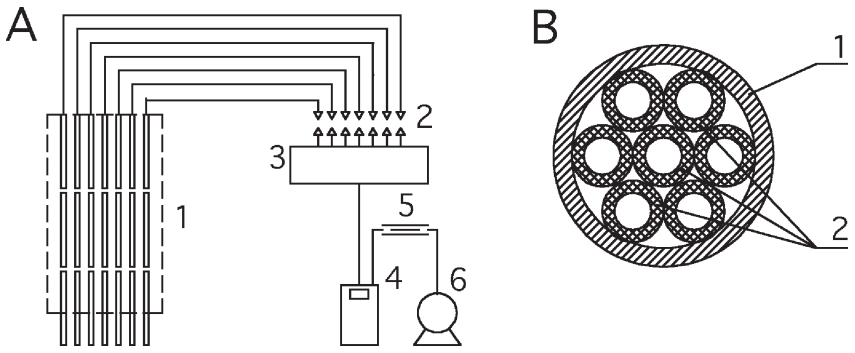

FIGURE 6. Systems for analyte enrichment utilizing cylindrical denuders: A: parallel system: 1 — denudation tubes, 2 — valves, 3 — manifold , 4 — gas meter, 5 — orifice (pressure reducer), 6 — pump; *such a system permits determination of several analytes differing in their chemical properties;* B: multichannel system: 1 — polymer tubes, 2 — metal tube; *this system permits determination of a single analyte (or group of analytes), while increasing the amount retained, thus lowering the detection limit.*

B. Basic Types of Denuders

Cylindrical denuders remain the basic design. Such a denuder is a tube with inner walls coated with a film of a suitable retaining medium.[55-62] In many designs, the cylindrical denuder is an element of a larger device. An example of such application is the combination of denuders in a parallel system, or in a so-called multichannel trap (Figure 6).[63-65]

A similar design, also permitting the application of high flow rates of the sampled gas is the denuder with a honeycomb-like cross-section.[66,67] A denuder of this type is built as a glass cylinder packed with a large number (more than 200) of hexagonal tubes of a very small diagonal. A specific version of cylindrical denuders is a device known under its acronym — INCAT (Inside Needle Capillary Adsorption Trap).[68] From the point of view of the manipulation technique, the method resembles solid phase microextraction (SPME).[69] The difference between the two lies in the placement of the sorbent layer, which in the SPME covers the exterior of the sampler needle, while in the method discussed — its interior. Pieces of capillary chromatographic columns have also been employed as denuders.[70,71]

The most frequently utilized designs are based on the annular denuders, due to their high effectivness of analyte retention (Eq. 7).[23,72,73] They are used in the aforementioned HVS systems (BOSS, IOVPS). Similar opportunities (for geometric reasons theoretical principles of both types are very close to each other) are offered by the parallel plate type denuders.

All the aforementioned types of denuders may be modified to work as wet denuders which may be built in the parallel plates type[74,75] (Figure 7), cylindrical,[76-78] or annular configuration (Figure 8). Basic advantage offered by these systems is possibility of their utilization for continuous measurements, for example, by combining them with ion-exchange liquid chromatography.[75]

The common feature of these denuders is the type of the retaining medium (a liquid). Components of the air stream come into a direct contact with the liquid sorbent. Usually, the gas stream and the absorbing solution enter the device in countercurrent: the stream of air is supplied to the bottom, while the liquid sorbent to the upper part of the device where, flowing downward, it wets the walls and forms a thin film on them. In the case of wet annular denuders, a horizontal arrangement is also known. In such a

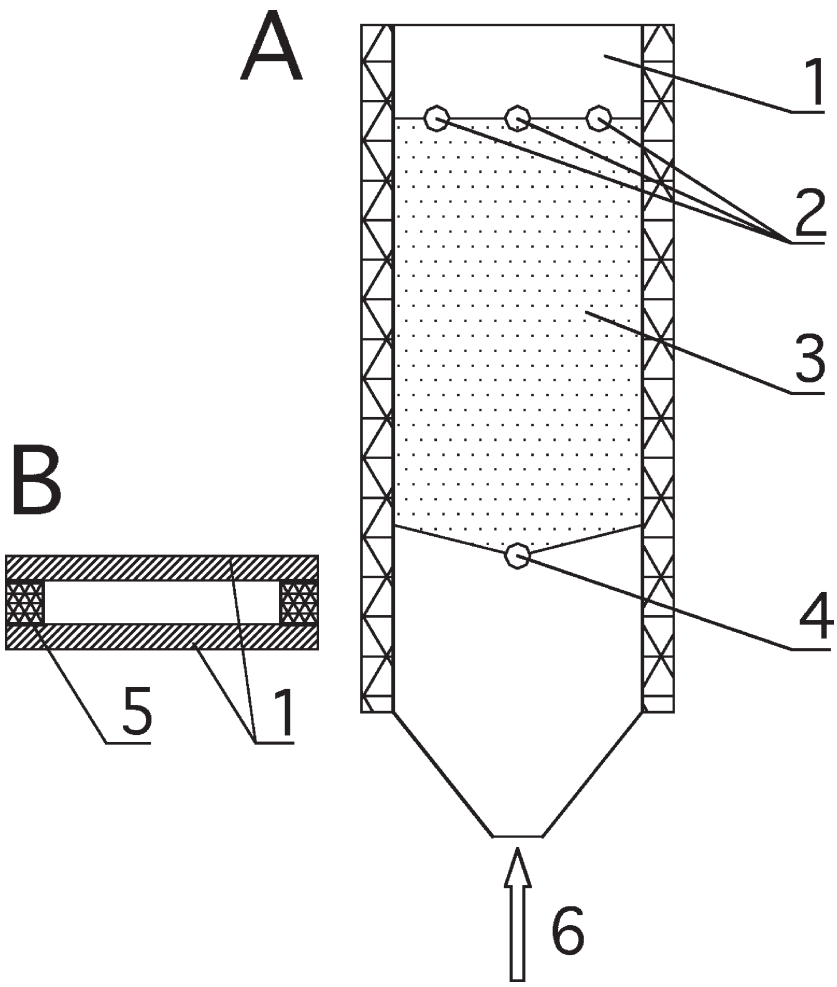

FIGURE 7. Schematic diagram of a wet denuder design (parallel plate type): (a) view from atop, (b) vertical cross-section; 1 — glass plate, 2 — inlet of absorbing liquid, 3 — porous silica layer, 4 — outlet of the liquid, 5 — spacer, 6 — air inlet.

case, the film of the sorption solution is formed by rotation of one of the two elements forming the annulus.[79,80]

A specific design, from the point of view of the retention mechanism, is represented by the diffusion scrubbers.[81-84] In denuders belonging to this type, the gas phase and the retaining medium phase are separated by a semipermeable membrane of specific properties. The analytes are transported to the medium in two processes: denudation toward the membrane surface and permeation through the membrane. Depending on the analyte, ion-exchange membranes (cationic or anionic)[85] or porous membranes[86] are employed. Geometry of such systems is usually annular. Two arrangements for gas sample passing are possible: in one — the gas sample is directed to the central cylindrical space; in the other — to the external annular space (Figure 9).[20]

Another specific design of wet denuders is the hanging drop device (Figure 10).[87,88] The drop of the absorbent has a precisely determined lifetime and geometric parameters. The composition of the absorbing solution depends on the properties of the analyte. Final determinations are carried out utilizing a

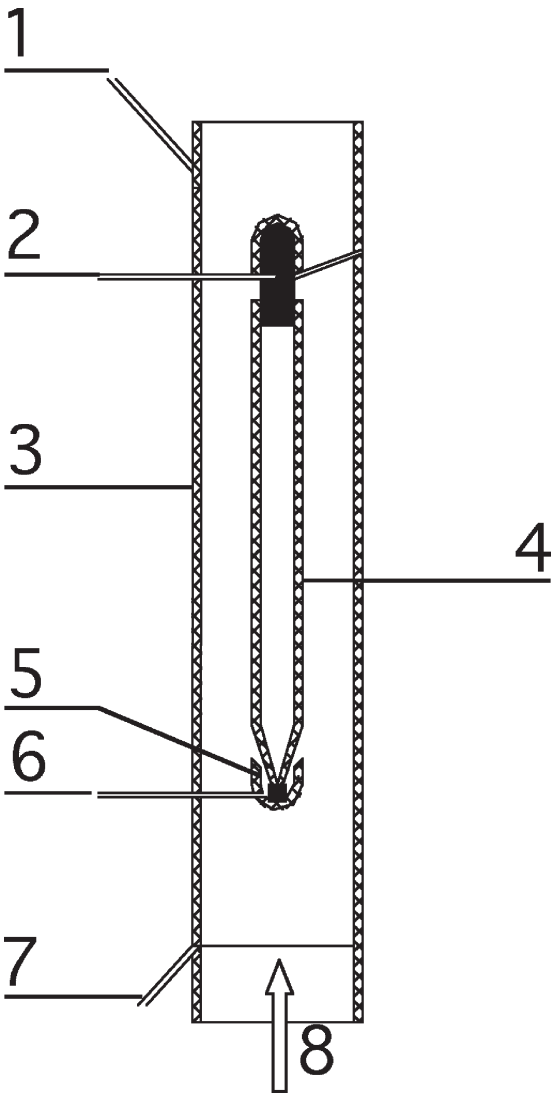

FIGURE 8. Schematic diagram of a wet annular denuder: 1 — inlet of absorbing liquid (onto the inner walls of the external tube), 2 — inlet of absorbing liquid (onto the outer walls of the internal tube), 3 — external tube, 4 — internal tube, 5 — collector of absorbate, 6 — absorbate outlet, 7 — external cylinder absorbate collector/outlet, 8 — air flow.

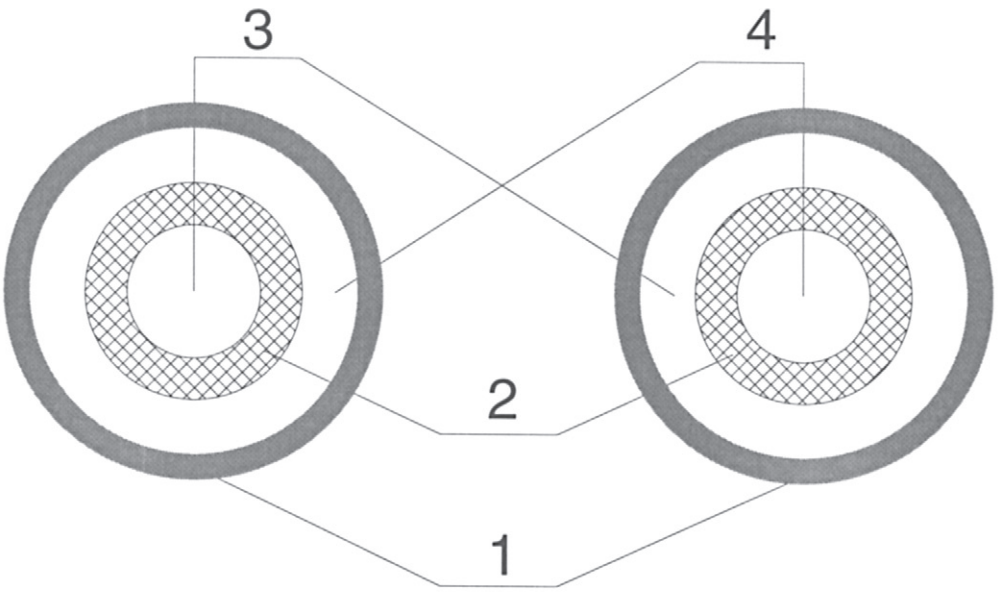

FIGURE 9. Schematic diagram of a diffusion scrubber: 1 — external steel tube, 2 — membrane, 3 — air stream, 4 — retaining solution.

detector consisting of a photoemitting diode (LED) — photodiode couple. The device can be operated with a detector placed at the vicinity of the drop formation site or on a capillary tube through which the droplet is transported by means of a suction pump.

Yet another type of denuders are devices with the retaining medium covering a suitable grid[89,90] (Figure 11) or a porous disc (frit).[91] In these arrangements the air stream direction is perpendicular to the disc surface.

So-called thermodenuders are another interesting example of the utilization of the denudation phenomena. The introduction of this design was the first step toward the automatization of the processes of isolation and enrichment of analytes from an air stream. Geometry of these devices is either cylindrical[92,93] or annular.[94,95] Essential differences lie in the types of the sorbents used and the method of liberation of analytes. Temperature-resistant compounds like tungsten and vanadium oxides (WO_3, V_2O_5) are used as the stationary phases. Thermodenuders can be operated in wide temperature range (up to 800°C). Programmed temperature desorption can be employed, thus permitting the simultaneous determination of several compounds. High temperatures, combined with frequently catalytic properties of the sorption layer (Au), permit to employ derivatization techniques.[96]

The classification of denuders based on their design features is presented in Figure 12.

C. Optimization of the Analyte Enrichment Stage

Analytical procedures, including analyte isolation and enrichment techniques, have remained in recent years under the strong influence of proecological trends. An example of this influence is the more and more common utilization of the solventless techniques. This approach can also be noticed in the denudation technique, in the wider utilization of the thermal method of liberation of analytes (primarily organic ones), although this method is limited to the "dry" stationary phases. The utilization of this technique for

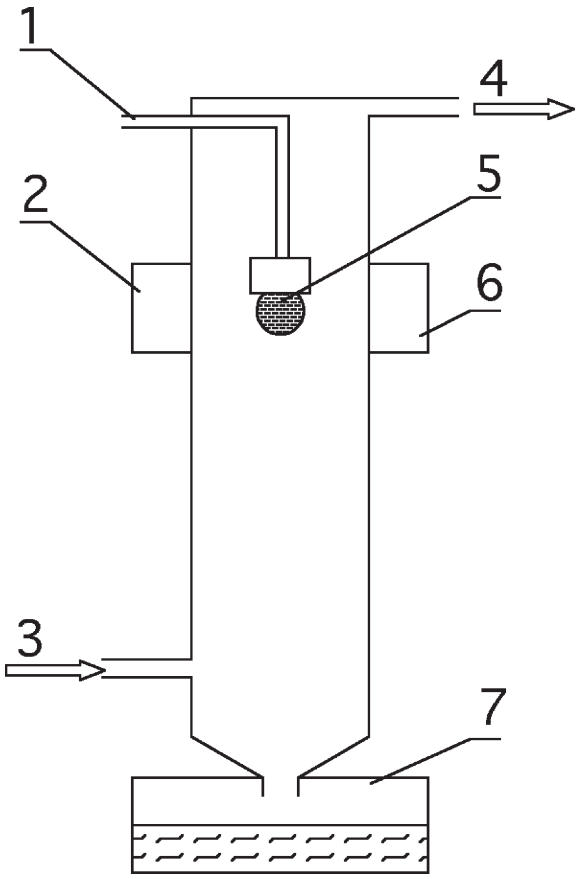

FIGURE 10. Hanging drop type denuder: 1 — supply of liquid, 2 — LED, 3 — air inlet, 4 — air outlet, 5 — hanging drop, 6 — photodiode, 7 — collecting tank.

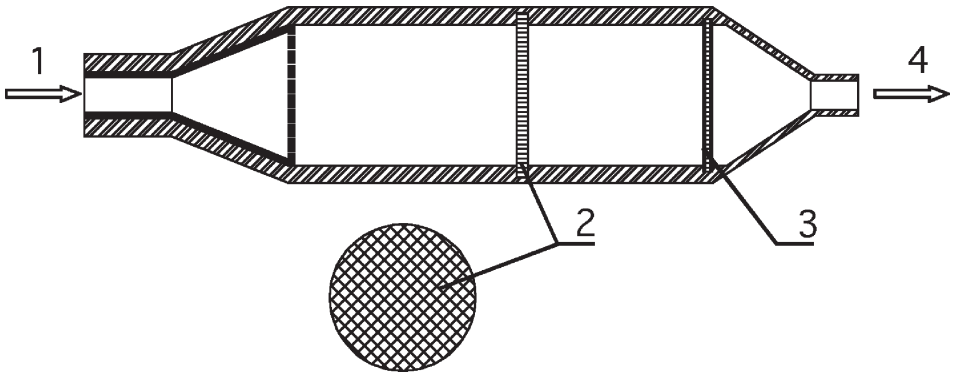

FIGURE 11. Schematic diagram of a diffusion denuder (screen type): 1 — air inlet, 2 — diffusion screen, 3 — filter, 4 — air outlet.

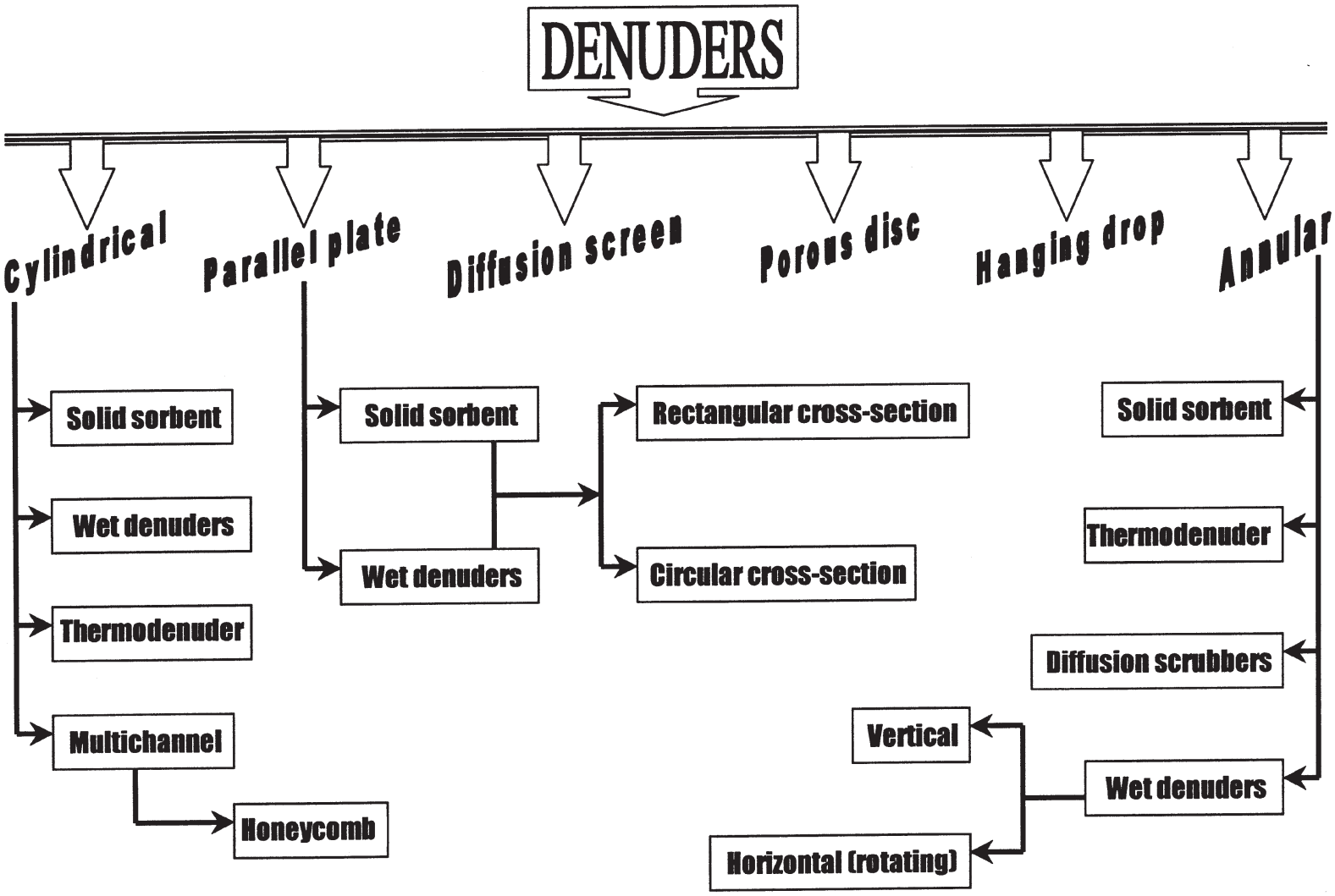

FIGURE 12. Classification of denuders according to their construction designs.

the enrichment of organic compounds leads to certain difficulties in the preparation of denuders.

As demonstrated in the discussion of the theory of enrichment (in the ESE technique), the efficiency of enrichment, and therefore the practical utility of the mehod, is primarily determined by the ratio of volumes of the two phases in the trap (Eq. 3). This parameter can be improved by increasing the thickness of the retaining film covering the walls of the denuder. Increasing the length of the trap can result in undesired effects:[97]

- increase in pressure drop along the denuder, that is, pressure difference between its inlet and outlet, leading to a necessity of including correction factors into the calculations to allow for the compression of air in the denuder;
- an analyte liberated in a thermal desorption process, fills the whole length of the denuder, resulting in a longer time in its introduction onto the head of a chromatographic column. To avoid this side effect, an additional step of sample focusing (*e.g.*, cryofocusing) must be introduced, leading to more complex instruments.

On the other hand, increasing the film thickness also met with serious difficulties. The static method (evaporation of a solution of the stationary phase) permit to obtain coatings up to slightly more than 10 μm.[98-100] The main obstacle in this method, as well as in the dynamic one,[101] is Rayleigh's instability effect.[102] This effect is caused by self-reorganization of the liquid surface, originating primarily from the surface tension forces. In this way, the originally uniform film assumes a shape of waves and droplets (Figure 13).

This effect increases significantly with the film thickness, the dependence being described by the relation:[103]

$$ln\left(\frac{D}{D_o}\right) = \gamma d_f^3 \rightarrow \frac{t}{12\eta a^4} \qquad (15)$$

where:

D/D_0 — ratio of the number of deformations after time t to the original number (at time t=0);

d_f — film thickness;
γ — surface tension;
t — time;
η — viscosity;
a — internal radius of the tube being coated.

Blomberg et al. have developed a technique permitting the obtaining of a uniform film of large thickness, based on a dynamic method with immediate crosslinking of the stationary phase.[104,105] This concept is shown schematically in Figure 14.

The tube being coated with the stationary phase is moved at a precisely controlled velocity in the direction opposite to the movement of the mercury plug that shapes the coating. The film is crosslinked at elevated temperature in max. 3 sec after its formation. This technical solution permitted obtaining films above 100 μm thick.[106]

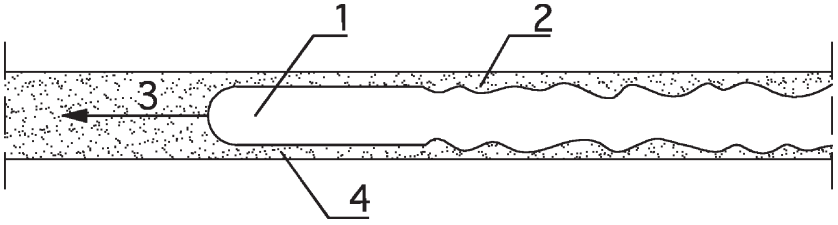

FIGURE 13. Self-reorganization of the stationary phase film after dynamic film formation: 1 — mercury plug, 2 — irregular coating, 3 — plug movement direction, 4 — uniform coating.

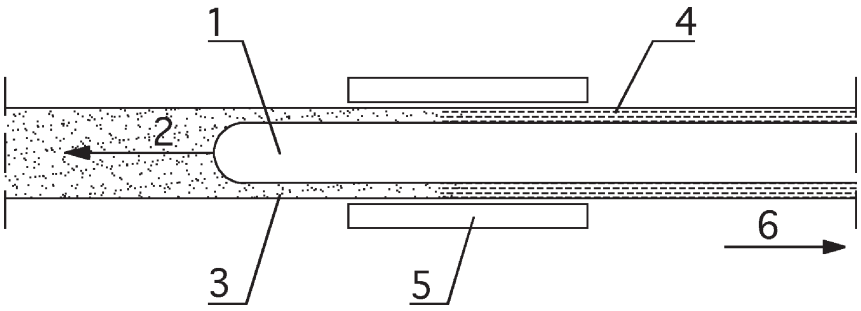

FIGURE 14. Coating the walls with a thick film of stationary phase followed by its immediate cross-linking: 1 — mercury plug, 2 - plug movement direction, 3 - uniform coating, 4 — cross-linked coating, 5 — oven, 6 — capillary tube movement direction.

Another approach to this problem was proposed by Burger et al.[107] Their method is one of placing inside the glass or steel main tube another tube made of polymer, which constitutes the coating. They used pieces of polysiloxane tubes used as medical drains. These tubes are stretched until reaching the appropiate external diameter, and subsequently frozen in liquid nitrogen. Thus, prepared tube is then inserted into the steel tube. When the tubes are heated back to ambient temperature, the polymer insert expands to its original dimensions and is fixed tight in the external steel tube. Manipulating the diameter and wall thickness of the original tubing, one can obtain coatings of different thickness, even above 200 μm.

V. PRACTICAL APPLICATIONS OF DENUDATION TECHNIQUE

The first use of a denuder in a study in atmospheric chemistry was described in a paper published in 1971. The aim of the study was the determination of the diffusion coefficient of SO_2 in air using a cylindrical denuder, whereas a denuder of annular geometry was used for the first time in the separation of gaseous and solid fluorine compounds. The latter device was built of three concentric cylinders coated with a thin film of $NaHCO_3$.

In recent years the interest in the denudation methods of analyte enrichment from the air and other gaseous mixtures has been growing significantly and steadily. Numerous publications describe the utilization of the technique for different analytical purposes, for example, drying gases or elimination of interfering substance from the gas samples.[108-122] In the last few years, several studies appeared that were devoted to the different aspects of denuder utilization in an analysis of liquid samples.[123-127]

In the past, denuders were used primarily for the determination of inorganic compounds in the atmosphere, whereas cases of the determination of organic compounds were rare. At present, the denudation technique is widely utilized for sampling both inorganic and organic analytes. Many papers deal with the possibility of denuder application in complex analyses of outdoor air.[128-132] The effectiveness of analyte enrichment from work site air was also studied.[133] An attempt was also made to determine the composition of automobile exhaust gases, a complex gaseous mixture containing relatively high levels of pollutants.[134]

Literature data on utilization of the different types of denuders in sampling analytes from an air stream are collected in Table 1.

TABLE 1. Examples of application of denuders in analytical chemistry.

No.	Analyte	Denuder type	Sorption mechanism					
			Adsorption on solid sorbent		Chemisorption on denuder walls		Absorption in solvent	
			sorbent	reference	sorbent	reference	sorbent	reference
1	HNO_3	cylindrical	nylon	135	Na_2CO_3	136, 137, 138, 139, 140, 141	ultrapure water	146, 147, 148
					Na_2CO_3 – glycerol	66, 142		
					KOH	143		
					NaCl	144, 145		
					KBr	145		
					WO_3	56		
		annular			Na_2CO_3	51, 149, 150, 151, 152, 153	Na_2CO_3 formic acid	173 79
					Na_2CO_3 – glycerol	91, 154, 155, 156, 157, 158, 159		
					$NaHCO_3$-glycerol	135, 160, 161		
					NaCl - eugenol	162		
					NaCl	151, 159, 163, 164, 165, 166, 167, 168, 169,		
					NaF	158, 170		
					citric acid	151		
					KOH	171		
					3-amine propylo-trietoksysilane	172		
		parallel plates					H_2O_2	74
		permeation membrane					ion-exchange membrane porous PTFE / water	174 45

No.	Analyte	Denuder type	Sorption mechanism					
			Adsorption on solid sorbent		Chemisorption on denuder walls		Absorption in solvent	
			sorbent	reference	sorbent	reference	sorbent	reference
1	HNO_3 (cd.)	thermodenuder			$MgSO_4$ $BaSO_4$ WO_3	175 175 92, 93, 135, 176, 177, 178		
		screen type (porous disc)			NaCl Na_2CO_3 –glycerol	179 180, 181		
2	HNO_2	cylindrical	nylon	135	Na_2CO_3 Na_2CO_3 –glycerol $NaHCO_3$	135, 182, 183, 184 66 185	ultrapure water water	78, 148 186
		annular			Na_2CO_3 Na_2CO_3 –glycerol $NaHCO_3$ $NaHCO_3$–glycerol	50, 149, 150, 152, 165, 168, 169, 187, 188 51, 155, 156, 158, 159, 163, 189, 190 135 160, 161	Na_2CO_3	173
		parallel plates			Na_2CO_3 –glycerol	191	H_2O_2	74
		screen type			Na_2CO_3	179		
3	NO_2	annular			Na_2CO_3 NaOH – quaiacol NaOH – eugenol KI	152, 159, 170 192, 193 162, 192, 193, 194 195, 196		
		liquid drop			Griess-Saltzmann reagent triethanolamine-TEA	197 198		

TABLE 1. (continued)

No.	Analyte	Denuder type	Sorption mechanism					
			Adsorption on solid sorbent		Chemisorption on denuder walls		Absorption in solvent	
			sorbent	reference	sorbent	reference	sorbent	reference
4	NH_3	cylindrical			oxalic acid	137, 139, 143, 199, 200, 201, 202, 203,	ultra pure water	146, 206
					oxalic acid – glycerol	184		
					citric acid	67,		
					citric acid – glycerol	66, 204		
					sulfuric acid	205		
					Na_2CO_3	142		
					H_3PO_4	136		
		annular			oxalic acid	144, 170, 207, 208	Na_2CO_3	173
					citric acid	73, 149, 150, 155, 159, 163, 187, 208, 209	ortho phosphoic acid	156
							H_2SO_4 (diluted)	211
					H_3PO_4	167, 208, 210	formic acid (pH=4)	79
		permeation membrane					$NaHSO_3$	212
							Nafion / H_2SO_4	85,
							porous membrane / pure water	82, 213
							/ H_2SO_4	156
		liquid drop					H_2SO_4 (diluted)	28
		thermodenuder			WO_3	56, 135, 175, 211, 214, 215, 216		
					V_2O_5	94, 211, 217		
		screen type (porous disc)			citric acid	180, 181		

No.	Analyte	Denuder type	Sorption mechanism					
			Adsorption on solid sorbent		Chemisorption on denuder walls		Absorption in solvent	
			sorbent	reference	sorbent	reference	sorbent	reference
5	H_2SO_4	thermodenuder			CuO	218		
6	SO_2	cylindrical	activated carbon	219	K_2CO_3 – glycerol Na_2CO_3 Na_2CO_3 – glycerol marble powder tetrachloromercu-rate (II) (TCM)	220 184, 221 135 222 143, 223	water	186, 224
		annular			Na_2CO_3 Na_2CO_3 – glycerol $NaHCO_3$ $NaHCO_3$ – glycerol tetrachloromercu-rate (II) (TCM)	50, 149, 150, 169, 170, 187 51, 66, 155, 157, 209 135 160, 225 158, 226	water HCHO	75 79
		parallel plates					water H_2O_2	75 227, 228
		permeation membrane					porous membrane / HCHO / H_2O_2	86 85, 224, 227, 229
		liquid drop					H_2O_2 / H_2SO_4	28
		thermodenuder			Cu / CuO	95		
		screen type (porous disc)			Na_2CO_3 Na_2CO_3 - glycerol	179 91		
7	$ClNO_2$, $ClONO_2$	cylindrical			KBr / KCl teflon	230 230		

TABLE 1. (continued)

No.	Analyte	Denuder type	Sorption mechanism					
			Adsorption on solid sorbent		Chemisorption on denuder walls		Absorption in solvent	
			sorbent	reference	sorbent	reference	sorbent	reference
8	H_2S	cylindrical			silver foil	149, 222		
		permeation membrane					porous membrane / NaOH	83
9	HCl	cylindrical	silica gel	231	NaF KOH Na_2CO_3	232 143 136		
		annular			NaF KOH Na_2CO_3-glycerol	167, 170 171 159, 209	Na_2CO_3 formic acid	173 79, 80
10	Cl_2	liquid drop					tetramethyl-benzidine (TMB)	29
11	HF	screen type (porous disc)			Na_2CO_3 – glycerol	180, 181		
12	H_2O_2	permeation membrane					porous membrane / acetic acid / water /HCl / p-hydroxyphenyl-acetic (PHPA)	233 81, 84, 86, 234 235 86
		annular			Ti(IV) – H_2SO_4	236	p-hydroxyphenyl-actic acid(PHPA)	79
13	CO_2	cylindrical			3 –metoxy-propylamine	237		

No.	Analyte	Denuder type	Sorption mechanism					
			Adsorption on solid sorbent		Chemisorption on denuder walls		Absorption in solvent	
			sorbent	reference	sorbent	reference	sorbent	reference
14	O_3	annular			eugenol KI polyisoprene Na_2CO_3-glycerol	130, 162 238, 239, 240 241 159		
15	Hg	cylindrical			silver gold KCl	89, 242, 243 242, 243,244, 245 89, 131, 246		
		annular			KCl	247		
		screen type (porous disc)			gold	89, 248		
16	HCHO	cylindrical			2-hydroxymethyl-piperidine (2-HMP)	249		
		annular			2,4-dinitrophenyl-hydrazine (2,4-DNPH)	250		
		permeation membrane					porous membrane / H_2SO_4 / water /1,3cyclohexane-dione	84, 86 251 252
		liquid drop					chromotropic acid / sulfuric acid	253
17	Tetraethyllead (TEL)	annular			ICl-ethyleneglycol-Carbowax 600	254		

TABLE 1. (continued)

No.	Analyte	Denuder type	Sorption mechanism					
			Adsorption on solid sorbent		Chemisorption on denuder walls		Absorption in solvent	
			sorbent	reference	sorbent	reference	sorbent	reference
18	Vaporized metal species ($HgCl_2$, Cd, $CdCl_2$, $ZnCl_2$, $PbCl_2$)	cylindrical			silver KCl	89 89		
		screen type (porous disc)			gold KCl	89 89		
19	Nicotine	cylindrical			oxalic cid	55		
		annular			benzenosulfonic acid (BSA) citric acid	255, 256 73		
20	Polycyclic aromatic hydrocarbons (PAH's)	cylindrical	methylsilicone stationary phase CP Sil-5 CB	257, 258, 259 260, 261				
		annular	silicone grease silicone oil / Tenax / pulverized graphitized carbon black (GCB) XAD-4	54, 262, 263 264 264 265				
21	Polychlorinated biphenyls (PCB's)	cylindrical	methylsilicone stationary phase XAD-4	258 265				
22	Organic peroxides (MHP, HMP)	permeation membrane					PP membrane Celgard X-20	81
23	Aniline	annular			oxalic acid	266		

No.	Analyte	Denuder type	Sorption mechanism					
			Adsorption on solid sorbent		Chemisorption on denuder walls		Absorption in solvent	
			sorbent	reference	sorbent	reference	sorbent	reference
24	Nitrobenzene	annular			platinum-lead alloy	267		
25	Vapour of organic compounds	cylindrical	activated carbon cross linked polydimethyl-osiloxane (PDMS) synthetic active carbon (Anasorb 747) divinylbenzene (DVB) methylsilicone stationary phase thick film silicone rubber PLOT-Q PLOT-S	60, 61, 68, 62 34 34 257, 258 59, 65, 103, 104, 107, 268, 269, 270 271				
		annular	Na_2CO_3- glycerol activated carbon silicone oil / Tenax / XAD-4	256 272 273 265				
		parallel plates	nylon nafion XAD II activated carbon	256, 274 256, 274 256, 274, 275 52, 191, 275, 276, 277, 278				

TABLE 1. (continued)

No.	Analyte	Denuder type	Sorption mechanism					
			Adsorption on solid sorbent		Chemisorption on denuder walls		Absorption in solvent	
			sorbent	reference	sorbent	reference	sorbent	reference
26	Acrylic acid	cylindrical			$NaOH/Ba(OH)_2$	279		
27	2,4,5-trichloro-phenol (TCP)	cylindrical					water (pH=8.5)	76
28	C_1-C_5 alifatic alkoholes	cylindrical					deionized water	280
29	α-hexachloro-cyclohexane β-hexachloro-cyclohexane hexachloro-benzene (HCB)	annular	silicone oil / Tenax	53, 281				
30	Isocyanate compounds (HDI, MDI, TDI)	annular			N-4-nitrobenzyl-N-1-propylamine tributylphosphate / 9-N-methylamino-methylanthracene (MAMA/TBP)	282 283		
31	C_1-C_3 carboxylic acids	cylindrical			Na_2CO_3-glycerol	284	water	186
		annular			KOH	167, 171		
		screen type (porous disc)			NaOH / triethanolo-amine (TEA)	90		
32	2-xylene, tetrachloroethane, dimethoxymethyl -phosphonate	cylindrical	Tenax TA	285				

No.	Analyte	Denuder type	Sorption mechanism					
			Adsorption on solid sorbent		Chemisorption on denuder walls		Absorption in solvent	
			sorbent	reference	sorbent	reference	sorbent	reference
33	Aldehydes & kethones	cylindrical					deionized water	280
		annular	2,4-dinitrophenyl-hydrazine (DNPH)	196, 286				
34	Propene	cylindrical	silica gel aluminium oxide marble powder	222 222 222				
35	acetylene	cylindrical	marble powder	287				
36	Organic healt hazardous substances (1,1,1-trichloro-ethane, trichloro-ethylene, butanone, cyclohexanone)	cylindrical	charcoal filtration paper	288				
37	C_1-C_5 – aliphatic amines	annular			acids: citric, ascorbic, salicylic, phosphoric, benzenesulfonic	289		
38	Pheromones	cylindrical	polysiloxane	290				
39	Plant volatiles	cylindrical	activated carbon	291				

VI. NEW TRENDS IN STUDIES ON APPLICATIONS OF DENUDATION TECHNIQUE

Numerous studies described in the literature confirm the feasibility of the application of the denudation technique for the isolation and enrichment of analytes. Despite the still widening spectrum of compounds that may be determined using denuders at the enrichment stage; the technique is not practically utilized on a wider scale. Also, a search for the best possible stationary phases cannot be treated as complete. Therefore, the nearest prospects for research in the field should include optimization leading to the selection of just several stationary phases (polar and non-polar). In this respect, an interesting suggestion may be utilization liquid crystal films as the retaining media in denuders. Capillary columns with such coatings are well known in GC practice,[135-138] but they have not yet been tested in denuders.

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