

Wet preconcentration techniques for "real time" determination of gaseous pollutants in ambient air

Z. Večeřa, P. Mikuška, J. Kellner and J. Navrátil

Abstract—The principle of mass transfer analytes in the wet effluent diffusion denuder (WEDD) and the aerodispersive enrichment unit (AEU) is explained. The spirits of WEDD and AEU are discussed in details and the application of these wet preconcentration techniques for "real time" determination of gaseous pollutants in ambient air, which are concerned of our long-time interest, is documented.

Keywords—aerosol accumulation, diffusion denuder, enrichment, gaseous pollutants, wet preconcentration techniques.

I. INTRODUCTION

The scientific and public concern about the origin, transport and adverse influences of atmospheric pollutants, which are both of inorganic and of organic nature [1], [2] on the biosphere caused that the enrichment techniques became an integral part of the trace analysis.

At classical procedures, inorganic compounds are preconcentrated by an absorption in impingers or are collected on special filters. Impinger preconcentration process is not suitable for concentrations below ppb (v/v) limit, partly because impingers contain relatively large amounts of the liquid when the accompanying effect of the increased liquid phase-volume decreases the enrichment degree and the sensitivity of the analytical method, and partly due to the necessity to employ the large volume of air during preconcentration step producing substantial loss of the liquid and so the reliability of determination of the given pollutant. Besides the gaseous compounds, the impingers also partly collect the aerosols from the atmosphere. The use of filters is limited their sorption capacities but the major problem is the

losses of volatile compounds through their dissociation or re-dissociation.

At present, inorganic trace gaseous pollutants are often preconcentrated in diffusion denuders which also allow the separation of gaseous pollutants in gas phase from those occurring in air in the condensed phase. A lot of times it was proved [3] - [5] that reliability of results obtained using diffusion denuders with various shapes of interception tubes are much better than reliability of results obtained by "traditional" techniques. The oldest type of the diffusion denuder is so-called "dry" denuder where on the sorbing wall an appropriate sorbent is deposited. The first "dry" denuder [6] used the sorbent oxalic acid for the determination of ammonia in ambient air. Unfortunately the preparation the sorbent covering the denuder tubes as well as extraction of adsorbed compounds are labor intensive, time-consuming and limit the application of "dry" diffusion denuders. During ambient enrichment courses of inorganic trace gaseous compounds also thermodenuders [7] - [10] have been used. This type of denuder utilize also the sorbent on the sorbing wall but on the contrary of classical "dry" diffusion denuders the collected pollutants are thermally desorbed under elevated temperature. The thermodenuders allowed automatic measurements but an unsatisfactory selectivity [8] - [10] is their crucial disadvantage.

In general, enrichment techniques for volatile organic compounds (VOCs) in the gaseous media are based on the sorption on solid materials, which are prevailing, and cryofocustion. From the point of view of the degree of enrichment, an adsorption is much more effective than the absorption process, respectively [11] - [13]. The adsorption procedure is used for preconcentration of organic trace compounds of interest in air at the range from units of ppt (v/v) to tens of ppb (v/v). The high values of the adsorption distribution constant complicate the recovery of analyte. The permanent and variable contents of water vapor [14], [15] present in air could be serious problem. After sampling the sorbent is stored, transported for analysis in the laboratory where the analyte is after the thermal desorption or liquid extraction analyzed by the gas chromatography or by gas chromatography-mass spectrometry. This relatively simple procedure fails at the determination of thermally unstable organic compounds (for example, organic compounds which

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Z. Večeřa is with the Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Veveří 97, 61142 Brno, Czech Republic (e-mail: vecera@iach.cz)

P. Mikuška is with the Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Veveří 97, 61142 Brno, Czech Republic (e-mail: mikuska@iach.cz)

J. Kellner is with the University of Defence, Civil Protection Department, 65 Kounicova, 662 10 Brno, Czech Republic (phone: +420973442097, fax: +420973443916, e-mail: josef.kellner@unob.cz).

J. Navrátil is with the University of Defence, Civil Protection Department, 65 Kounicova, 662 10 Brno, Czech Republic (e-mail: josef.navratil@unob.cz).

include sulfur in their molecule or biogenic substances like terpenes) or the compounds that undergo chemical or catalytic reactions with the sorbent. It was found that unsaturated compounds such as styrene, cyclohexane or monoterpenes adsorbed on sorbents can react for example with ozone during sampling of ambient air leading to the diminution of analyte concentration and formation of oxidated reaction products [16]. When liquid cooling media have been used (Ar, N₂) during preconcentration by cryofocusing, ambient gases (vapores) are physically concentrated together with VOCs. When this "concentrate" is heated for sample transfer or injection onto the gas chromatographic system, above mentioned reactions can occur [17].

In the course of determination of VOCs in the atmosphere the "dry" type of denuders have been also used. Activated charcoal, Tenax or various silicon phases for example [18] - [20] were applied to form the "active wall" of the denuder. After sampling procedure organic compounds were thermally desorbed or extracted by the suitable solvent from the denuder and analyzed.

The common methodic disadvantage of all above mentioned enrichment procedures is their discontinuity. It means we receive only integral information concerning the changes of analyte concentration in the atmosphere in certain time interval. A few other enrichment methods allowing continual enrichment and on-line analysis have been described. However, some of them like the joint condensation of organic trace analytes with vapor of a solvent [21] or absorption of gases and vapors in a film of water co-condensing on a cooled surface [22] have not been applied in practice. The diffusion scrubber (DS), a membrane-based diffusion denuder introduced by Dasgupta [23], was the first instrument used in practice for the continual preconcentration and on-line analysis of gaseous pollutants. In DS the absorption liquid flows inside a semipermeable microporous polypropylene membrane tube and the analyzed air flows round the porous tube. The DS was completely automated for the measurement of inorganic gases soluble in water [24] - [28]. Unfortunately, the material of porous tube restricts the application of the diffusion scrubber only to water-soluble compounds. Finally, its long-term use is limited by blocking of pores of the collecting tube.

Much higher collection efficiency than the diffusion scrubber and no affect by plugging of membrane pores provide so-called wet diffusion denuders where the absorption liquid is in the direct contact with analyzed air. The simplest version of wet effluent diffusion denuder (Figure 1.) is represented by a cylindrical borosilicate glass tube [29].

The interior wall of this tube is modified to form a layer of porous soft glass that is highly wettable. The absorption medium flows down on the wall in a thin layer under the influence of gravitation while the analyzed air moves upward countercurrently under laminar flow conditions. The more complicated construction of wet diffusion denuder is a rotating wet annular denuder [30] - [32]. This type of denuder rotates along its longitudinal axis and the absorption liquid is kept on

the "active" walls of the denuder by means of the centrifugal and adhesion forces. The problem is that the rotating wet annular denuder contains a relatively large amount of the liquid (up to 15 ml) causing a decrease of the detection limit of compounds of interest in air.

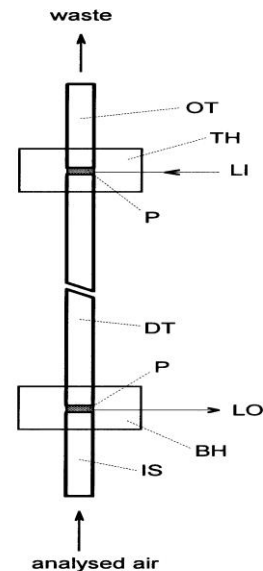


Fig. 1 The scheme of the wet effluent diffusion denuder
DT - denuder tube, IS - inlet subduction zone, OT - outlet tube, P - porous O-ring (PTFE), LI - liquid inlet, LO - liquid output, TH - top head, BH - bottom head.

The aerodispersive enrichment unit [33] is another enrichment equipment (Figure 2) with direct contact of absorbing liquid with analyzed air. This device operates on the principle of balanced accumulation of pollutants from the gas phase by means of polydispersive aerosol. The polluted air is sucked through jets in which are positioned stainless steel capillaries for delivery of absorption liquid into enrichment unit. By means of an ejection effect of the air the sorption liquid is dispersed. The polydispersive aerosol comes out of the jet in the narrow beam into the condensation part of the enrichment unit where coagulates as a consequence of quasi-adiabatic expansion and collision with the slanting barrier. Sampling procedure allows automatic measurements without artifacts.

II. THE PRINCIPLE OF MASS TRANSFER ANALYTES IN WEDD AND AEU

In general, the wet effluent diffusion denuder and the aerodispersive enrichment unit are mass exchangers with continuous contact of phases where mass transfer occurs in the whole volume of apparatus. The intensity of analyte mass transfer ($\langle j_{An} \rangle_t$) in the direction of the collection in the wet effluent diffusion denuder and the aerodispersive enrichment unit can be described by the relationship (1):

$$\begin{aligned} \langle j_{An} \rangle_t &= - [r D_A / (d \langle X_A \rangle_t / dn) - r \langle X_A V_n^* \rangle_t \\ \langle j_{An} \rangle_t &= - [J_D - J_T] \end{aligned} \quad (1)$$

where V_n^* denotes the fluctuation of a mixture weighed according to the mass amount, D_A is the diffusion coefficient of analyte, r is the density of the medium, X_A is the analyte concentration in the gas phase and $(d \langle X_A \rangle_t / dn)$ is the analyte concentration gradient. In case of the wet effluent diffusion denuder the intensity of mass transfer can be described only by the diffusion component of the mass flow (J_D) while at enrichment by means of the balanced aerosol accumulation the turbulent component of the mass flow (J_T) is the most important.

The behavior of gaseous analyte in the diffusion denuder was for the first time described by Gormley and Kennedy [34]. More details about diffusion denuders can be obtained from review papers of Ali and co-workers [35] or Zdráhal *et.al.* [36].

At constant temperature, pressure and under the steady state laminar flow conditions when the denuder wall is the perfect sink for the analyte and there is no destruction (res. changing) of analyte the collection efficiency of analyte is related to a multiexponential equation [37] (2):

$$1 - C/C_{iG}^0 = 1 - (B_0(k) \exp(-\beta_0^2(k) X) + B_1(k) \exp(-\beta_1^2(k) X) + \dots + B_n(k) \exp(-\beta_n^2(k) X))$$

$$X = 2 D_A L / V_m \delta^2 \quad (2)$$

where C is an average concentration of gaseous analyte at exit of the denuder, C_{iG}^0 is the entering concentration of gaseous analyte, D_A is the diffusion coefficient of analyte, L is a length of denuder channel, B and β are variable dependent on parameter k which is determined by the geometry of denuder tube, V_m is the medium linear velocity of a gas and δ is the hydraulic diameter of the tube. For the cylindrical denuder the following relation is valid (3):

$$C/C_{iG}^0 = 0.8191 \exp(-14.6272 \Delta) + 0.0976 \exp(-89.22 \Delta) + 0.0325 \exp(-227.84 \Delta)$$

$$\Delta = \pi D_A L / 4 U_G \quad (3)$$

U_G expresses the flow rate of the analyzed gas through the denuder. For a planar denuder, formed by two plates, Gormley (38) derived equation describing diffusion of analyte in gas flow into unlimited channel constructed by two parallel plates ($b \gg a$) (4):

$$C/C_{iG}^0 = 0.9104 \exp(-15.08 \Delta_p) + 0.0531 \exp(-171.44 \Delta_p) + \dots$$

$$\Delta_p = D_A L b / 4 a U_G \quad (4)$$

where a is a half of channel height and b is a width of the channel. The collection of analyte in the annular denuder is described by the next equation [37] (5):

$$C/C_{iG}^0 = B_0(k) \exp(-\beta_0^2(k) X) + B_1(k) \exp(-\beta_1^2(k) X) + \dots + B_n(k) \exp(-\beta_n^2(k) X)$$

$$X = \pi D_A L (d_o + d_i) / 4 U_G (d_o - d_i) \quad (5)$$

where d_o and d_i are diameters of tubes of the annular denuder.

The degree of preconcentration (D), defined as a ratio of the analyte concentration in the liquid phase to the analyte concentration in the gaseous phase before to the entrance to enrichment equipment, is providing the most important information about the ability of the enrichment equipment to preconcentrate the analyte from the gaseous phase to the liquid one. For the wet effluent diffusion denuder operating under optimal conditions the degree of preconcentration is expressed by the relationship (6):

$$D = C_{iL} / C_{iG}^0 = U_G / U_L \quad (6)$$

where U_L is volume flow rate of liquid through the denuder and C_{iL} is the concentration of the analyte in the liquid phase leaving the denuder.

The mathematical solution of the analyte accumulation by the aerodispersive enrichment unit operating on the principle of the balanced accumulation of pollutants from the gas by means of the polydispersive aerosol has been described by Večeřa and Janák [33] in 1987. Reliable operation of this device has been verified by preconcentration of both model compounds and real samples from air with the excellent agreement. The theoretical prediction of enrichment by balanced accumulation is based on fact that after an enlargement of the liquid surface by formation of the polydispersive aerosol of the liquid the adsorption of analytes [39] - [42] becomes a driving process for the distribution of the analyte between the gaseous and the liquid phase because the adsorption rate is at least by two orders of magnitude higher than for the absorption one. After the contraction of the aerosol surface by coagulation when the adsorbate is included into the bulk of absorbing liquid matrix it is possible to neglect the effect of the effective rate of reaching the thermodynamic equilibrium on distribution of analyte between the gas phase and the liquid phase being in the aerosol form.

The next relation describes the collection efficiency of pollutants at the balanced accumulation (7)

$$1 - C/C_{iG}^0 = Q_{iL} / Q_{iG}^0 = (K_A U_L / U_G) / (1 + K_A U_L / U_G) \quad (7)$$

where K_A is the distribution constant of the analyte between the liquid and gaseous phases, U_L and U_G are volume flow rates of the liquid and the gas phase, respectively, through the aerosol enrichment unit. Q_{iG}^0 and Q_{iL} are amount of the analyte entering the enrichment unit in the gas phase and amount of

the analyte which is found at the liquid concentrate leaving the aerodispersive enrichment unit. The degree of preconcentration for aerosol enrichment unit is defined by equation (8):

$$D = C_{iL}/C_{iG}^0 = K_A/(1 + K_A U_L/U_G) \quad (8)$$

Although the application of the aerodispersive enrichment unit allows the continuous transfer of the analyte from gas phase into the liquid phase for its on-line analysis, on the contrary to the wet effluent diffusion denuder, the aerodispersive enrichment unit is not enable to distinguish gaseous pollutants from those which are adsorbed on particles or presented in the atmosphere in the condensed phase.

III. PRACTICAL APPLICATION OF WET PRECONCENTRATION TECHNIQUES IN OUR LABORATORY

The principle of the aerodispersive enrichment unit (Figure 2) has been applied in monitors of sulfur dioxide and ammonia. A monitor for the continuous measurement of sulfur dioxide in air is based on the enrichment of SO₂ by polydisperse aerosol of deionized water with on-line detection of hydrogensulfite in the film of the condensate on the wire-gauze conductivity sensor [43] - [45]. Low response delay, good sensitivity (1 ppb (v/v)) with a small relative error $\pm 5\%$ at 4 ppb (v/v), high selectivity (CO₂ does not interfere at common concentrations while interference by NO_x and H₂S is acceptably low) allow monitoring of sulfur dioxide in ambient air. Calibration graph is non-linear but the curve is fitted by the linear equation of the second order whose coefficients can be easily calculated.

The analysis of the concentrate leaving the aerodispersive enrichment unit by an ion selective electrode was applied in the monitor [46] enabling real-time continuous measurement of ppm (v/v) concentrations of ammonia at cowsheds atmosphere with relative error $\pm 2\%$ for 30 ppm (v/v) and $\pm 8\%$ for 10 ppm (v/v). The calibration graph is linear. Interference of aliphatic amines has been found negligible.

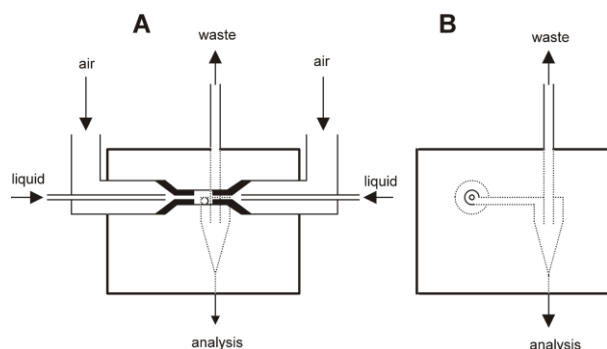


Fig. 2 The contemporary construction of the aerosol enrichment unit (Aerosol counterflow two-jets unit). (A) front view; (B) side view.

The balanced accumulation of gaseous pollutant on polydisperse aerosol has been also explored in the ambient air detector, a chemiluminescent aerosol detector (CLAD). The chemiluminescent aerosol detector has been used in monitoring of ozone and the nitrogen dioxide in air. In case of nitrogen dioxide [47] the reaction of nitrogen dioxide with an alkaline solution of luminol was the source of chemiluminescent radiation. The detection limit of nitrogen dioxide is 0.01 ppb (v/v). The calibration graph is linear up to 400 ppb (v/v). After the substitution of luminol solution by the solution containing eosin Y with gallic acid it is possible to monitor ambient ozone [48]. The detection limit for ozone is 0.3 ppb (v/v). The response of the detector is linear for the ozone contents up to 349 ppb (v/v). No significant interferences from other common gaseous pollutants occurring in usual concentrations in the atmosphere were found at both CLAD detectors mentioned above.

The idea of the aerodispersive enrichment unit we used for construction of device for continuous measurement of the soluble fraction of atmospheric aerosols [49]. This type of aerosol collector is employing a liquid at laboratory temperature for continuous sampling of atmospheric particles. This particles collector operates on principle of a Venturi scrubber. Sampled air flows at high linear velocity through two Venturi nozzles (atomizing" the liquid to form two jets of polydisperse aerosol of fine droplets situated against each other (Figure 2). Counterflow jets of droplets collide, and within this process, the aerosol particles are captured into dispersed liquid. Under optimal conditions (air flow rate 5l/min and water flow rate of 2 ml/min), aerosols down to 0.3 μm in diameter are quantitatively collected. Operation this device in combination with on line detection devices allows in situ determination of water soluble aerosol species (e.g. NO₂⁻, NO₃⁻) with limit of detection for nitrite and nitrate 28 and 78 ng/m³, respectively.

The first applicable wet effluent diffusion denuder, the denuder with falling film of absorption liquid, has been constructed at Texas Tech University in the beginning of nineties in co-operation of Prof. Dagupta and Dr. Večeřa. This WEDD has been used for the simultaneous determination of nitric acid and nitrous acid in ambient air with time resolution 11 minutes [29]. Both acids are quantitatively collected into deionized water and preconcentrated on anion resin bed and after that corresponding anions are separated on IC column. After conversion of nitrate to nitrite on cadmium reductor, nitrite reacts with the Griess-Saltzman reagent and formed product was determined spectrophotometrically. The detection limit for nitric acid and nitrous acid is 230 and 80 ppt (v/v), respectively. Latter on, this method has been used for the measurement of indoors nitrous acid level produced by open flame sources [50] cylindrical wet effluent diffusion denuder was used in the trials of rapid and sensitive measurement of ambient nitrous acid [51]. Nitrous acid is continuously collected into a thin film of deionized water flowing down the inner wall of denuder tube and absorbed nitrous acid is, after

sampling by 50 μl loop of six way valve, on-line detected as nitrite anion by means of the chemiluminescent FIA system [52]. This technique did not exhibit significant interference due to gaseous co-pollutants. The detection limit of nitrous acid is 0.5 ppt (v/v) and time resolution is about 20 seconds.

The cylindrical WEDD has been also applied for the determination of VOCs in ambient air and workplace. 2,4,5-trichlorophenol was quantitatively collected into deionized water (adjusted to pH 8.5) [53] while less polar 1,4-dichlorobenzene is preconcentrated into 1-propanol with 96 % collection efficiency [54]. Both pollutants are determined on-line in denuder effluent using a pico-HPLC with C_{18} stationary phase and UV detection with time resolution 7-9 min. The detection limit for 2,4,5-trichlorophenol and 1,4-dichlorobenzene is 0.09 and 1 ppb (v/v), respectively.

In the paper [55] the wet effluent diffusion preconcentration technique for determination of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 1-pentanol is presented. The compounds are continuously collected into a thin film of water flowing down onto the inner wall of the cylindrical wet effluent diffusion denuder. The concentrate is analyzed by gas chromatography. This technique could be applicable for continuous monitoring of trace amounts of $\text{C}_1\text{-C}_5$ alcohols in air. Detection limits are as low as $1 \mu\text{g}/\text{dm}^3$.

The wet effluent diffusion denuder technique, for the determination of α -pinene, β -pinene, s-limonene, α -phellandrene, camphene and Δ^3 - carene in air has been tested [56]. These monoterpenes were continuously preconcentrated into a thin film of methanol (ethanol, 1-propanol and heptane) flowing down the inner wall of the cylindrical wet effluent diffusion denuder. The concentrate were analyzed by GC-FID and GC-MS, respectively.

The last version of our wet denuder, applicable for long lasting out door utilization has been used within two project: "Real time" analytical chemistry of forest non-methane hydrocarbons using wet effluent diffusion denuder technique (Grant agency of CR 203/98/0943) and Emissions of biogenic compounds from *Picea abies* [L.] under the long-term influence of increased carbon dioxide levels (Grant agency CR 526/03/1182).

The paper [57] describes sensitive and fast method for the determination of nitrous acid in air. The method combines a continuous collection of nitrous acid into a thin film of deionized water in a cylindrical wet effluent diffusion denuder and on-line analysis of collected nitrous acid at the denuder concentrate employing a flow-injection analysis (FIA) where nitrous acid is oxidized into peroxyxynitrous acid and a chemiluminescent light emitted during the reaction of peroxyxynitrite with luminol is detected. The time resolution is 70 s and the response time is 164 s. The calibration curve is linear over 4 orders of magnitude (0,045-450 ppb HONO). The WEDD-FIA technique has been applied to the measurement of nitrous acid in urban air and its credibility has

been verified in intercomparison campaign FIONA (Intercomparisons of Observations of Nitrous Acid, Valencia, 10.5.- 28.5.2010).

Wet effluent diffusion denuder has also been used in the course of measurements [58] of nitrous and nitric acids onboard the research vessel Aegeon in the Aegean Sea (Project INCO Copernicus, EVK2-CT-1999-0052 SUB-AERO, 5. "Subgride Scale Investigations of Factors Determining the Occurrence of Ozone and Fine particles). Mixing ratios of both nitric and nitrous acids in the ambient air of the Aegean Sea were mainly below 50 ppt (v/v). The data also showed a number of short pollution episodes with changes in the concentration of reactive nitrogen compounds. These episodes were correlated with pollution plumes originating from boats upwind, at short distance, from the R/V Aegeon. The measurements revealed the importance of nitrous and nitric acids for the transport of nitrogen to marine biota in busy ship lanes.

IV. CONCLUSION

Within last 20 years has been confirmed many times that wet preconcentration techniques based on accumulation of the analyte in aerosol and the denuders with falling film of absorption liquid are continuous enrichment techniques allowing the on-line analysis of both organic and inorganic gaseous pollutants. These wet preconcentration techniques can be used for monitoring of ambient trace compounds, even for measurement of their fluxes at high sensitivity.

The WEDD, AEU device are fairly robust for field applications. The idea of the aerodispersive enrichment unit has also been used for construction of device for continuous measurement of the soluble fraction of atmospheric aerosols.

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