

Unconventional use of adsorption for enrichment of impurities in gases

Jaroslav Janák

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences,
Leninova 82, CS-611 42 Brno, Czechoslovakia

Abstract - An enrichment technique has been developed on the basis of adsorption of trace components present in gases on the surface of finely dispersed liquid droplets. Using a stream of liter volumes of air, microliter volumes of water condensate have been produced giving an enrichment by a factor of 10^4 both for trace gases such as SO_2 and for vapours of high boiling substances such as 2-naphtol simultaneously. Long term tests of the technique have been performed in field monitoring of SO_2 in air with continuous signal on ppb level.

INTRODUCTION

Frequent task of contemporary trace, resp. ultratrace analysis of impurities in gases, for instance in atmosphere, is to increase the content of trace in the sample to be analyzed to the level at which the given analyte can be determined reliably by available methods (ref. 1). Another not less important task means to look for such procedures which would make it possible to perform trace analysis continuously.

Wide investigations, describing sorption processes in heterogenous systems where one of the phases is gaseous and, in solid and/or liquid phases, adsorption plays a direct or a complementary role in the other phase, were performed and reviewed comprehensively in gas chromatography (ref. 2-4), particularly by Soviet schools (ref. 5,6).

THEORETICAL

In general it is possible to differentiate a gas-solid (adsorbent) binary system and gas-liquid-solid (adsorbent) ternary system (cf. Fig. 1).

The former case of the sorption, A, is characterized by the distribution coefficient, K (related to the known Gibbs function $\Delta G^0 = -RT \cdot \ln K$). The rates of adsorption and desorption are then characterized by rate constants k_1 and k_2 and the transport of the analyte is controlled by the diffusion coefficient in the gaseous phase D_G .

In the latter gas-liquid system, B, in which absorption is expected, a substantial influence of the solid phase (adsorbent) must be admitted. Then a complex distribution function to which correspond distribution coefficients K' , K'' , and K''' , characterizing the degree of the analyte dissolution in the liquid, adsorption on the liquid surface and adsorption of analyte under the liquid film, respectively, must be taken into consideration. If the surface of the liquid phase increases in comparison with its volume and if chemical similarity of the liquid phase and the analyte decreases, the influence of the coefficient K'' manifests in the complex distribution function.

Discussing the velocity at which sorption and desorption proceed, we can consider in the majority of cases of the equilibria controlled by a linear isotherm that $k_1 = k_2$, whereas in the case of three active phases the situation is more complicated. In the first approximation the usual situations are characterized in Fig. 1. The diffusion of the analyte in this system is controlled by coefficients D_G and D_{Liq} with $D_G \gg D_{\text{Liq}}$.

It holds in general that the adsorption in the predominating majority of cases is, in comparison with the dissolution process, significantly more thermally exposed, hence $\Delta G_{\text{ads}}^0 > \Delta G_{\text{diss}}^0$ and $K > K'$. Similarly, the adsorption rate is faster by the order of magnitude than that of absorption, hence $k_1 > k_1'$ (cf. ref. 7).

If we start from these facts, we can imagine a liquid medium of such chemical quality and with a surface of such a size that adsorption becomes the controlling mechanism of sorption without greater effects of chemical structure of analytes.

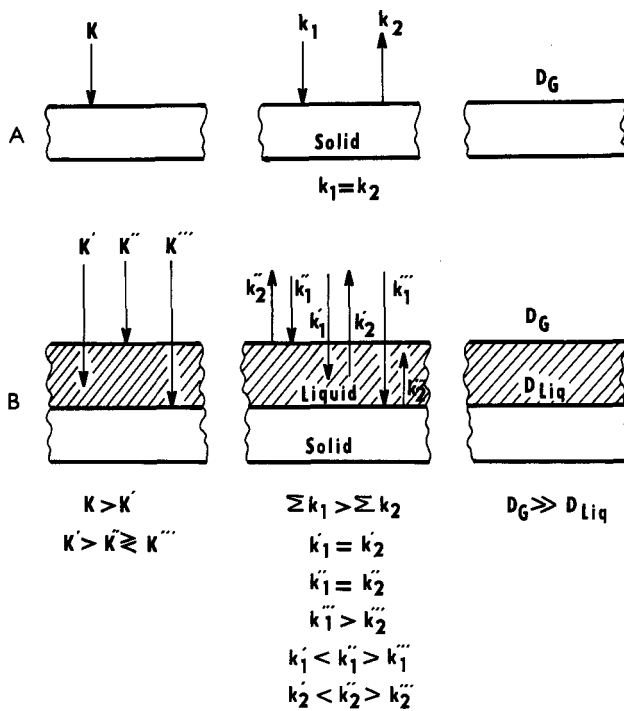


Fig. 1.
Simplified model of sorption processes
in binary and ternary systems

K - distribution coefficient,
k - sorption rate constant,
D - diffusion coefficient

A Gas-solid system
B Gas-liquid system

The subject of the present contribution is an experimental evidence that by applying water in the form of dispersed droplets of micron diameters, we are able to create a sufficiently large surface which is accessible to the adsorption of compounds regardless their volatility and/or their ability to dissolve in water. This is significant for a wider scale of trace compounds which are in question in the analysis of atmosphere, however, also in the analysis of other gaseous media. Moreover, an interfering effect of always present and variable content of water vapour in atmosphere can thus be fairly eliminated, since the water vapour content in atmosphere is the source of serious problems in enrichment of trace impurities by a simple adsorption (conservation methods) (ref. 8). Furthermore, equipment can be designed relatively easily that operates continuously and is capable of providing continuous signal to a particular analyte, to a group of analytes or to more analytes simultaneously.

For the enrichment mentioned above we can write for the mass balance of the mass of analyte i :

$$Q_{iG}^0 = Q_{iLiq} + Q_{iG} + Q_{iSurf} \quad (1)$$

In the equation Q_{iG}^0 is the total amount of analyte before the entrance to enrichment unit, Q_{iLiq} is the amount of analyte dissolved in the liquid phase, Q_{iG} is its amount in the gaseous phase after sorption, and Q_{iSurf} represents the amount of analyte adsorbed on the surface of aerosol of liquid. After contraction of the aerosol surface by coagulation, the adsorbate is included by a suitable means into the liquid bulk and a subsequent establishment of the equilibrium between the analyte in liquid and gaseous phases occurs. Due to a negligible size of the gas-liquid interphase after the coagulation of the aerosol, the term Q_{iSurf} in relationship (1) can be neglected. Derivation of equations (2) and (3) and general solution was published earlier (ref. 9). The following expression was derived for Q_{iLiq}

$$Q_{iLiq} = \frac{K_{iLiq} \cdot u_{Liq}/u_G}{1 + K_{iLiq} \cdot u_{Liq}/u_G} \cdot Q_{iG}^0 \quad (2)$$

where u represents particular flow velocity of liquid or gaseous phase through the unit and K_{iLiq} is the partition coefficient of the analyte in liquid phase.

The dependence between the initial analyte concentration in analyzed gas (air), C_{iG}^0 , and the analyte concentration in liquid concentrate leaving the unit, C_{iLiq} , can be expressed

$$C_{iG}^0 = C_{iLiq} \cdot \frac{T_2 \cdot p_1 (u_G + K_{iLiq} \cdot u_{Liq})}{T_1 \cdot p_2 \cdot u_G \cdot K_{iLiq}} \quad (3)$$

where p_1 and p_2 are gas pressures before the entrance to enrichment unit and inside it, respectively. T_1 is the temperature of the gas entering the enrichment unit and T_2 is the temperature of the coagulated aerosol inside this unit.

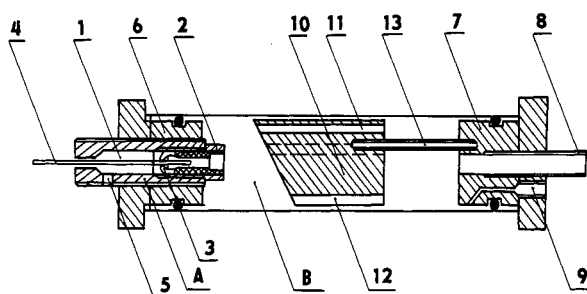


Fig. 2. Schematic design of the enrichment unit

A - nebulizer section, b - condensation section, 1 - boaring, 2 - jet, 3 - jet support, 4 - capillary, 5 - inlet hole, 6 - front face, 7 - back face, 8 - crossing channel, 9 - sampling channel, 10 - coagulation barrier, 11 - holes for changing conditions for aerosol coagulation, 12 - channel connecting the sampling device, 13 - adjusting connection

EXPERIMENTAL

The enrichment unit (Fig. 2) consists of a nebulizer section (A) and a condensation section (B).

The nebulizer comprises a special jet into which enters coaxially a capillary, through which the analyzed gas is sucked into the unit.

The condensation section is composed of a glass cylinder closed with faces. The nebulizer is screwed into the front face; connections to a vacuum pump and to a sampling device pass through the back face. The main part is a skew barrier on which the aerosol beam coagulates. Constructional and functional details are described elsewhere (ref. 10). Experimental data: At an underpressure of $0.21 \cdot 10^5$ Pa (160 mm Hg) the volume flow rate of the analyzed gas is ca. 5 L/min. and the volume flow rate of the liquid condensate is 100 - 800 μ l/min.

The dependence of enrichment efficiency for analytes with very different physical and chemical properties on their distribution coefficient for three different values of the flow rate ratio u_G/u_{Liq} is illustrated in Fig. 3. Experimental values for accumulation of organic substances from air were obtained for o-cresol (Δ) (system with water) and toluene (\square) (system with n-decane) at a concentration of $1 \cdot 10^{-6}$ g/L and for 2-naphtol (\circ) (system with water) at $1 \cdot 10^{-9}$ g/L of air. A very good correspondence of the experiment with the course of the function $Q_{iLiq}/Q_{iG} = f/K_{iLiq}$ confirms that the enrichment unit has a wider application area both from the point of view of analytes with different surface tensions (water 72 dyn.cm⁻¹, n-decane 29 dyn.cm⁻¹) and with different physical and chemical properties (low boiling hydrocarbon, high boiling phenol). Satisfactory results have been found also for the enrichment of atmospheric sulphur dioxide at ppb level (ref. 10,11) and ammonia at ppm level (ref. 12).

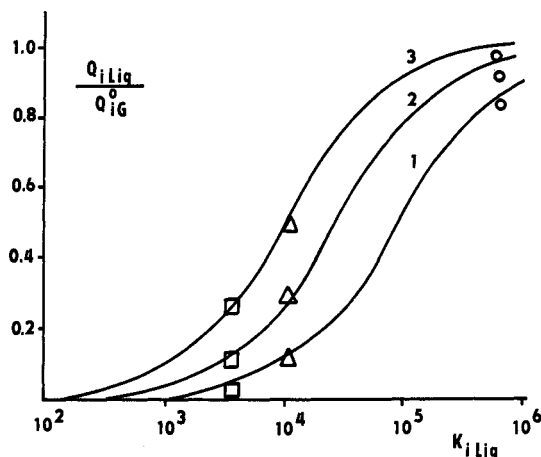


Fig. 3. Graphic presentation of theoretical course of the dependence of recovery Q_{iLiq}/Q_{iG} on the distribution coefficient K_{iLiq} for different flow rate ratio u_G/u_{Liq} . 1 - $5 \cdot 10^3$, 2 - $1 \cdot 10^4$, 3 - $5 \cdot 10^3$. Data found experimentally: \square toluene, Δ cresol, \circ 2-naphtol.

CONCLUSIONS

The described technique represents an unconventional way of using the adsorption of volatile traces of different chemical nature on the surface of a liquid for their enrichment from litre volumes of gases to microlitres of liquid.

The technique has been verified for longterm monitoring of differently volatile and soluble substances (2-naphtol and SO₂) from air to water with the enrichment by a factor of 10⁴. The response time is usually tens of seconds maximally. The unit is sufficiently robust to be used in field monitoring.

The principle is able to give new goals in trace analysis if FIA methods are used as tandem techniques.

Regulating the contact time of the gaseous and the aerosol phases we can influence the course of dissolution of adsorbed compounds and degree of their possible dissociation in the liquid, which we can use for a selective determination of different analytes by means of a simple detection method, e.g., by conductivity measurements.

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