Volatile organic compounds evaporation chamber for the simulation of gas effluents in laboratory research

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A device for mixing air with a pollutant (*e.g.*, volatile organic compounds) is presented, which is based on principles of evaporation and diffusion. A wide-necked flask containing an aluminium cylindrical body, allows the evaporating area to be preset to 5.75 cm^2 or 23.03 cm^2. The distance from the evaporating surface to the region of passage of the air is adjustable between 0 and 8 cm, which allows to assay a wide range of evaporation flows (for toluene: 1.5 to 200 mg/minute).

Introduction

Approximately 1.6 million tonnes of toxic chemicals are released annually into the environment without any treatment, of which 65% are released into the air (Ritchie and Hill, 1995).

US EPA (United States Environmental Protection Agency) has been trying to reduce the emission of volatile organic compounds (VOCs), such as toluene, xylene, benzene and phenol, which are in general considered photo-reactive. They are common pollutants of surface and underground water, as well as of gas streams. For US EPA, they are priority environmental pollutants.

The purpose of the present mixing chamber is to supply a controllable (with the desirable accuracy) flow of pollutant, to be incorporated, without risks, in the air stream, in order to simulate a gas effluent in lab research (*e.g.*, biodegradation of toluene).

Effluent simulation in laboratory

Several systems to study the biological removal of VOCs have been used to simulate gaseous effluents in the lab:

Syringe pump

A low rotation pump, coupled with a syringe, injects the liquid pollutant into the air stream, allowing very low solvent flow rates, such as 19 μL benzene/h (Haigler *et al.*, 1992). Both the air and pollutant flows may be independently controlled.

Air bubbling

It is the simplest but also the less adequate way, since it is impossible to control the evaporation flow. This device is acceptable when a single constant flow is needed (Ritchie and Hill, 1995).

Injection

This system is a kind of Venturi tube, working by suction. It works only with relatively high solvent concentrations, the air and solvent flows being difficult to control independently.

Another device proposed by Ottengraf *et al.* (1986) consists of a system using capillary tubes and Venturi tubes, being the flow of pollutant controlled by pressure.

The present mixing device is based upon the principle of equimolar counterdiffusion.

Equimolar counterdiffusion (EC)

A special case of EC with convection occurs when only one of the gases diffuses, while the other one is stagnant (Figure 1). A liquid (A) evaporates and diffuses through a gas (B). If the gas is air, whose flow removes all the fluid arriving at the top of the tube, the partial pressure of A, leaving the tube, is kept close to zero. If the air is stagnant inside the tube, P, T and the distance to the surface are kept constant and if the ideal gas law is applicable, then (Geankoplis, 1983)

$$N_A = \frac{D_{AB}PS}{RTz} \ln\left(\frac{P}{P - p_A}\right) \qquad (Eq\ 1)$$
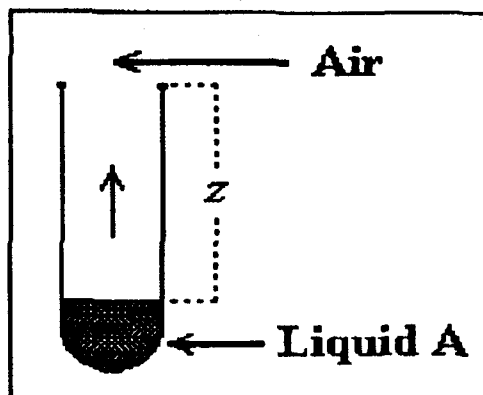
Figure 1 Vapour diffusion in stagnant air.

being N_A the stationary flux of A (mol/s); D_{AB} the diffusivity of A in B (m²/s); P and T the total pressure (Pa) and the temperature (K) of the system; S and z the area of the section (m²) and the distance (m) from the top to the liquid surface; R is the universal gas constant; and p_A is the vapour pressure (Pa) of A, at the system temperature. By varying S and T it is possible to obtain a great variety of evaporation flows, independently of the air flow. However, if the air is not stagnant, then the evaporation flows are much higher than those predicted by Eq. 1. This is the principle which the mixing chamber is based upon.

The Antoine equation (Reid *et al.*, 1977) can be used to determinate p_A.

The value of D_{AB} is also T and P (supposed constant) dependent. According to several authors (Perry and Green, 1984), D_{AB} is proportional to a power of T between 1.5 and 2.0. With known experimental values of D_{AB}, we can easily determine n and α of the equation:

$$D_{AB} = \alpha T^n \qquad (Eq\ 2)$$

Mixing chamber

The chamber, designed and built to investigate the biological removal of VOCs, is basically a glass wide-necked flask with an internal volume of about one litre, containing a cylindrical body in aluminium, with three communicating cavities and a glass tube coupled with a scale for the observation of the liquid level (Figure 2).

Four holes were drilled on the aluminium top cover of the flask. One of the holes is for the air inlet, another is for the gas mixture outlet, another one for the solvent

feeding and the last hole allows the passage of the lever suspending the float, which is used for level control. The liquid feeding is done through a permanently submerged 6 mm OD stainless steel tube (Figure 3). The central cavity enables to increase the evaporating surface and can be sealed with a metallic piece, which completely covers that surface (and the corresponding volume), thereby allowing the evaporating surface to be of 23.03 cm² or 5.75 cm². All the cavities are connected through a hole of 4 mm diameter. The evaporating surfaces were designed to assure continuous evaporation flow. The maximum flow attained with the minimum area (level zero of the scale) must be close to the value obtained with the maximum area, for a level between eight and nine.

The cavity where the float is inserted allows its vertical movement. When the float moves downwards, the articulated system connected with it makes the detection of its movement possible, since a metallic cylindrical piece approaches an electro-magnetic detector (Telemecanique™ XS 1M 30 MA 230). The detector sends an electric signal to a timer which opens an electro-valve, for a predetermined period (*e.g.*, half a second). While the electro-valve is open, the positive hydrostatic pressure in the washing bottle compels the solvent to enter the mixing chamber. To avoid excess pressurization, the compressed air in use has to cross a compacted cotton filter. The float level can be regulated in a range of 8 cm. The electro-magnetic detector sensitivity allows the metallic float to travel at most 1.5 mm, before being detected.

Both the inverted test tube (where the articulated system is placed) and the flask cover are appropriately sealed with rubber o-rings. A couple of screws prevents the cover from being pulled out, by the air pressure.

The glass tube for the level visualization is 4 mm OD. Behind it, there is a scale in a metallic web, numbered from 0 to 9 units (subdivisions of 0.2), for the level readings.

A baffle was placed below the air inlet into the chamber to avoid direct contact between the air and the solvent. The air flux, inside the chamber, showed turbulent behaviour. Therefore, the actual evaporation flow proved to be higher than the predicted by Eq. 1.

The performance of the present mixing system was assayed with toluene as solvent. Utilizing the values of diffusivity (D_T) of toluene (Table I), found in the literature (Perry and Green, 1984) and the model
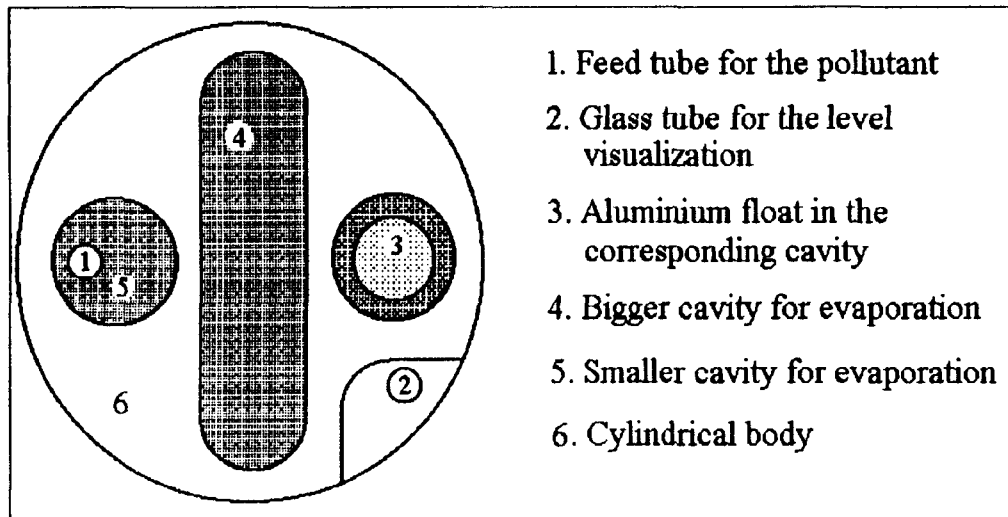
1. Feed tube for the pollutant

2. Glass tube for the level visualization

3. Aluminium float in the corresponding cavity

4. Bigger cavity for evaporation

5. Smaller cavity for evaporation

6. Cylindrical body

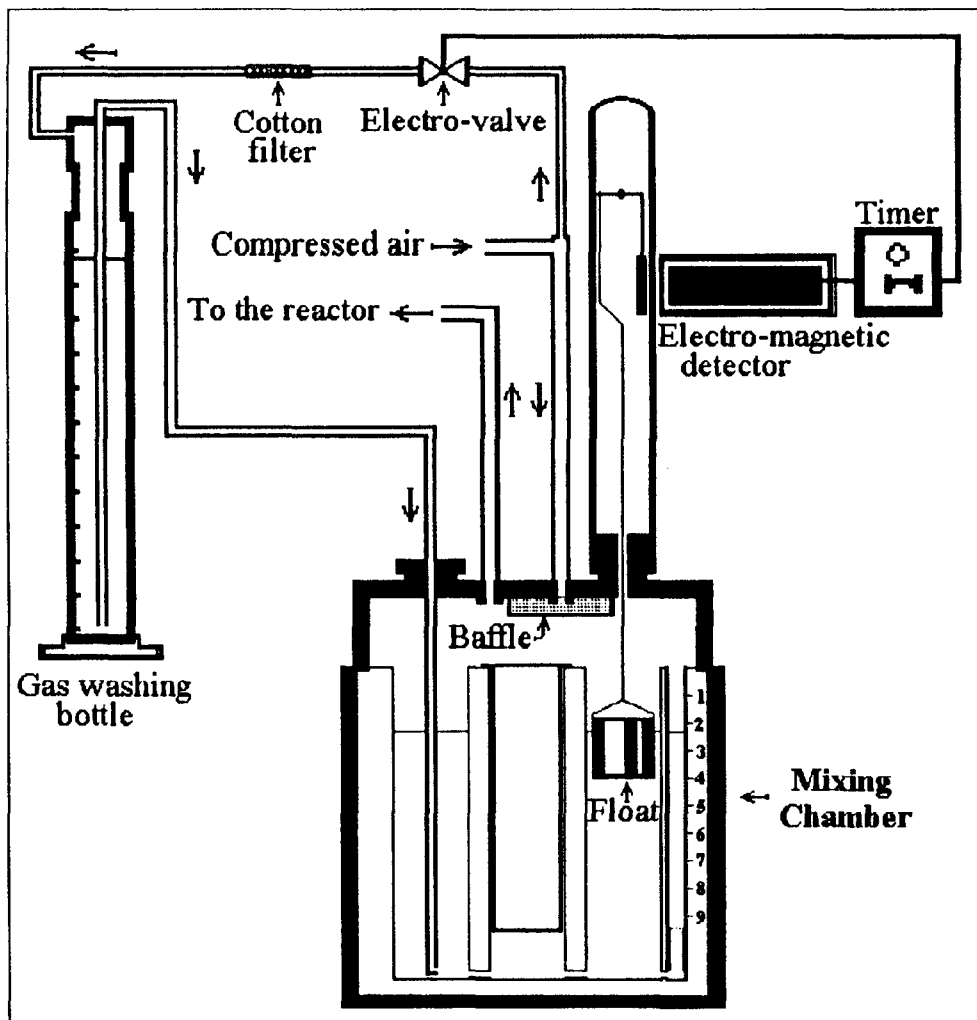**Figure 2**   Upper view of the cylindrical body.

Figure 3   The system for simulation of polluted air (frontal cut view).

Table I Diffusivity (1 atm), density (saturated liquid) and Antoine equation constants for toluene

Diffusivity		Density		
T (°C)	$D_T \times 10^6$ (m2/s)	T (°C)	ρ (g/mL)	Antione constants
0	7.6	17	0.870	A=16.0137 mmHg
25.9	8.6	20	0.867	B=3096.52 K mmHg
30	8.8	27	0.861	C=−53.67 K

pointed out by Eq. 2, the following SI relation (P = 1 atm) was obtained:

$$D_T = 1.67 \times 10{-9} \times T^{1.5} \qquad (Eq\ 3)$$

Starting with Eq. 1 and Antoine equation and making the necessary substitutions for 1 atm and 28°C ($\rho = 0.860$ g/mL), Eq. 4 is obtained for the evaporation flow of toluene, N_T, in mg/min, as a function of the surface (m²) and the distance to the top where the vapour is removed (m). The prevailing atmospheric temperature, during the procedures of calibration was 28°C.

$$N_T = 86.4 \frac{S}{z} \qquad (Eq\ 4)$$

The air from a compressed air system flows through one of two rotameters (Fischer & Porter[TM]; high flow: FP D10 A1197 A; small flow: FP 10 A6131 NA 2B), covering all the needed flow range.

The mixing chamber was calibrated with toluene. Four different flows of air (15%, 50% and 85% of the small rotameter and 40% of the big one) were tested with several evaporation flows, manipulating the evaporating area and the level of toluene in the chamber.

The connections between the chamber and a mass spectrometer (MS) (Bioquad[TM], Ledamass, England) were performed with 6 mm diameter stainless steel tubes, coupled to a heating resistance ($40 < T < 50$°C) to avoid the occurrence of moisture in the gas current. The MS spectra made possible to quantify the practical flows.

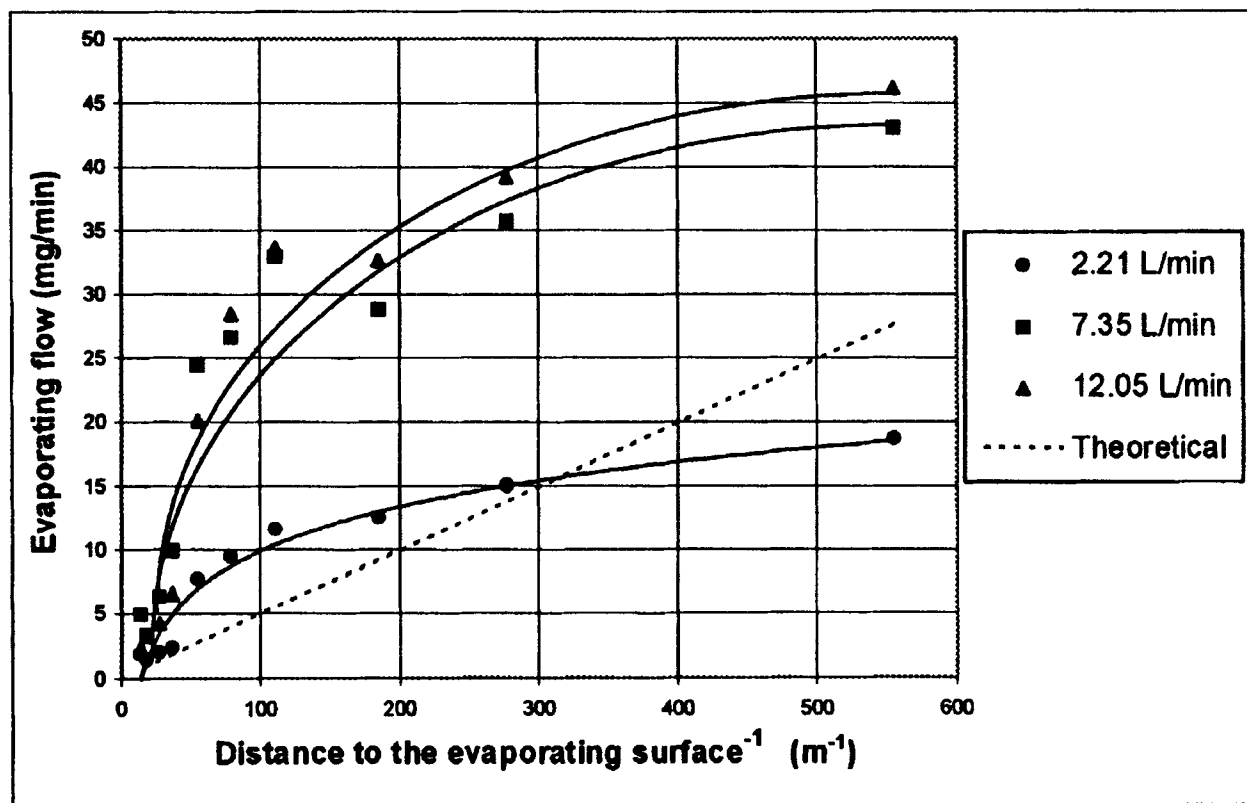The quantification method of toluene was based on the sensitivity of toluene related to nitrogen. To determine

Figure 4 Experimental and theoretical curves for toluene evaporation flow with an evaporating area of 5.75 cm² ($P = 1$ atm and $T = 28$°C).
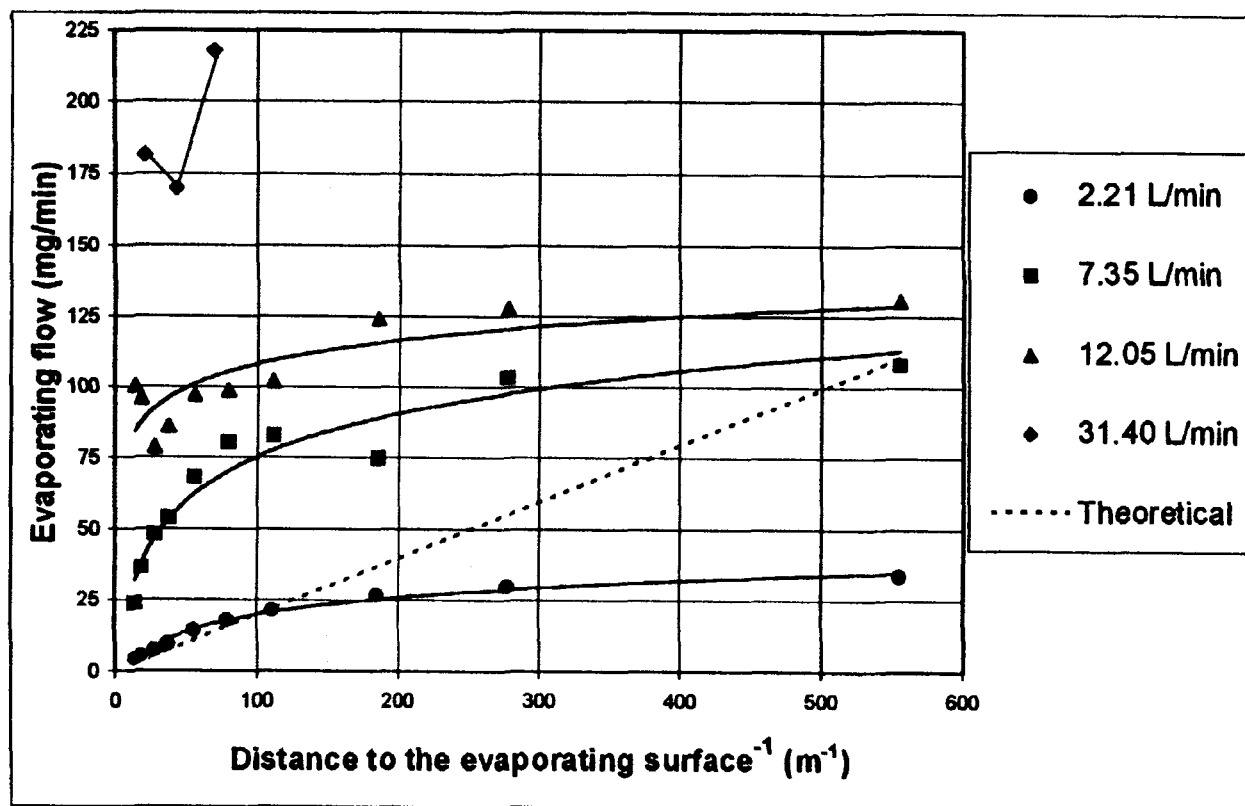
Figure 5 Experimental and theoretical curves for toluene evaporation flow with an evaporating area of $23.03\,cm^2$ ($P = 1$ atm and $T = 28°C$).

the relative sensitivity, toluene was evaporated for a time long enough to have a good estimation of the evaporation flow. Once the flow of air was known it was possible to determine the concentration and, with the respective record, to calculate the relative sensitivity, with the known percentage of nitrogen in the air current.

To calculate the evaporation flows thirteen runs were made, with times varying between 44 minutes and several days. Both 91 and 92 peaks were monitored, being the sensitivity based on peak 91 (bigger amplitude).

Eq. 4 represents the theoretical evaporation curve. The experimental ones were drawn following the calibration records of the mixing chamber (Figures 4 and 5).

The differences observed between the experimental and theoretical curves are a consequence of the agitation of the liquid surface and of the air above it, caused by the air current, which are more evident for bigger flows and when the liquid surface is closer to the top.

Due to the lesser agitation, the theoretical and experimental results approach again for bigger distances. With the minor air flow (2.21 L/min) experimental results are close to the theoretical ones, which again could be expected due to a lesser turbulence effect.

The three runs with the maximum assayed flow (31.40 L/min) showed the biggest difference.

Conclusions

Even having deviations from the expected, the theoretical formulation was important for the definition of the most suitable evaporation surface and tube depth. In any case, by controlling the liquid inlet, with an adequate calibration, this device proved to be very useful to assay for a range of solvent concentrations varying from 40 to more than 5000 ppm, in the case of toluene, which demonstrates its large versatility.

References

Geankoplis, C.J. (1983), Transport Processes and Unit Operations, Second Edition, Allyn and Bacon, Inc. Boston.

Haigler, B.E.; Pettigrew, C.A.; Spain, J.C. (1992). *Appl. Environm. Microbiol.*, 58, 2237–44.

Ottengraf, S.P.P.; Meesters, J.J.P.; van den Oever, A.H.C.; Rozema, H.R. (1986). *Bioprocess Engineering*, 1, 61–9.

Perry, R.H.; Green, D. (1984), Perry's Chemical Engineers' Handbook, Sixth Edition, McGraw-Hill International Editions, Chemical Engineering Series, New York.

Reid, R.C.; Prausnitz, J.M.; Sherwood, T.K. (1977), The Properties of Gases and Liquids, Third Edition, McGraw-Hill Chemical Engineering Series, New York.

Ritchie, B.J.; Hill, G.A. (1995). *J. Chem. Tech. Biotechnology*, 62, 339–344.