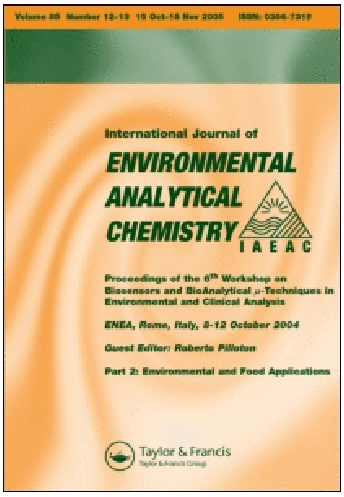

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DEVELOPMENT AND PERFORMANCE CHARACTERISTICS OF A CAPILLARY DOSAGE UNIT WITH IN SITU WEIGHT SENSOR FOR THE PREPARATION OF KNOWN AMOUNTS OF GASEOUS VOC's IN AIR

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This paper describes the design, performance and operation of a home-made capillary dosage unit with in situ weight sensor. This continuous injection technique is developed to produce dynamic gas phase calibration mixtures of VOC's in a diluent gas at occupational hygiene levels. A new advance in the technique allows the calculation of the amounts of pollutants emitted into the carrier gas, directly from the gravimetric measurements.

This is achieved by a built-in weight sensor which is monitored without interfering with the injection process. The survey of the capillary dosage unit(s) is managed by a microcomputer which automatically lists the amounts of pollutants introduced into the diluent gas. The capillary dosage technique thus becomes related directly to a primary standard.

The homogeneity and stability of the test gas generated is shown to be better than 1% relative standard deviation over periods of up to 24 hours. The VOC concentrations in the manifold are known with a total uncertainty of between 2 and 3%.

KEY WORDS: Continuous injection method, capillary dosage unit, primary standard, gaseous VOC's.

INTRODUCTION

One of the problems frequently encountered in the research on analytical methods for occupational hygiene survey involves the dynamic generation of gas phase calibration mixtures. It has become common practice to use, whenever possible, the permeation method or the diffusion method. The permeation tube method[1,2,3] has some limitations. Any material with a room vapour pressure over 20.10E5 Pa cannot be used in a permeation device. To achieve reasonable permeation rates (0.1–4 μg/min), it is necessary for the permeant material to have a vapour pressure of at least 0.2.10E5 Pa at its operation temperature. The diffusion tube offers an alternative[4,5] for compounds with low vapour pressures at room temperature.

For many volatile organic compounds (VOC's) which are commonly sampled workplace pollutants, the methods mentioned above have too low emission rates and cannot be used whenever a high gas flow ($\geq$200 l/min) is required or whenever ppm levels of workplace pollutants are desired in high gas flows. High gas flows are often necessary for intercomparison exercises with many participants performing active and passive sampling simultaneously.

In these cases the use of a continuous injection technique[6] is imperative. The use of a pressure difference across a well defined capillary offers the possibility to prepare a wide range of gaseous VOC's in high carrier gas flows at occupational hygiene levels. To provide a primary standard for these applications, the capillary dosage units are modified in such a way that it becomes possible to measure on-line the weight loss of the emitted pollutants without interfering with the injection process.

Moreover, this technique offers the ability to create, in a dynamical way, synthetic gas mixtures with pollutants at ppb and ppm levels simultaneously in the same carrier gas flow. The method offers an important reduction in the cost-effectiveness of gas generation systems since there is no need to follow up emission rates as is necessary for permeation and diffusion tubes; there is no need for a temperature-controlled (±0.1°C) oven.

CAPILLARY DOSAGE UNIT

The dynamic generation of gaseous VOC's at occupational hygiene levels in a carrier gas is achieved by fluid injection through a glass capillary. The fluid is thermally heated, evaporated and injected dynamically into a gas stream. This technique is known as capillary dosage. The new approach to this technique consists of a built-in weight sensor which allows to calculate the injected amounts of pollutants while the injection process is still going on. This ensures that the concentration of the gas mixture is known at any time during the injection even when charging fluctuating concentration levels at short intervals.

Equipment

Figure 1 shows the schematic representation of a capillary dosage unit. The main components are: a glass capillary, a pressure reducer, a miniature weight sensor and a stainless-steel housing. A pressure difference between both ends of the capillary forces the liquid through it. At the upper end of the capillary, the fluid is flash-heated and evaporated. The resulting vapour is injected dynamically into a primary flow of mass flow controlled nitrogen. The nitrogen enters at the low pressure side of the capillary and transports the evaporated compound to the main stream of the carrier gas. At the higher pressure side, the capillary is immersed in the liquid. The reservoir containing the liquid is connected to a weight sensor which allows a continuous measurement of the liquid consumption at any time during its injection process.

In order to obtain a broad concentration range of workplace air pollutants, a set of glass capillaries is available with internal diameters of 15, 20, 25, 35, 55, 70 and 90 μm. The length is fully dependent on the configuration of the capillary dosage units and is standard 22 cm. Commonly used pressure differences across the capillary are between 0.1 and 5 bar relative. The pressure in the capillary dosage unit is measured by a digital pressure indicator with a sensitivity of 0.001 bar.

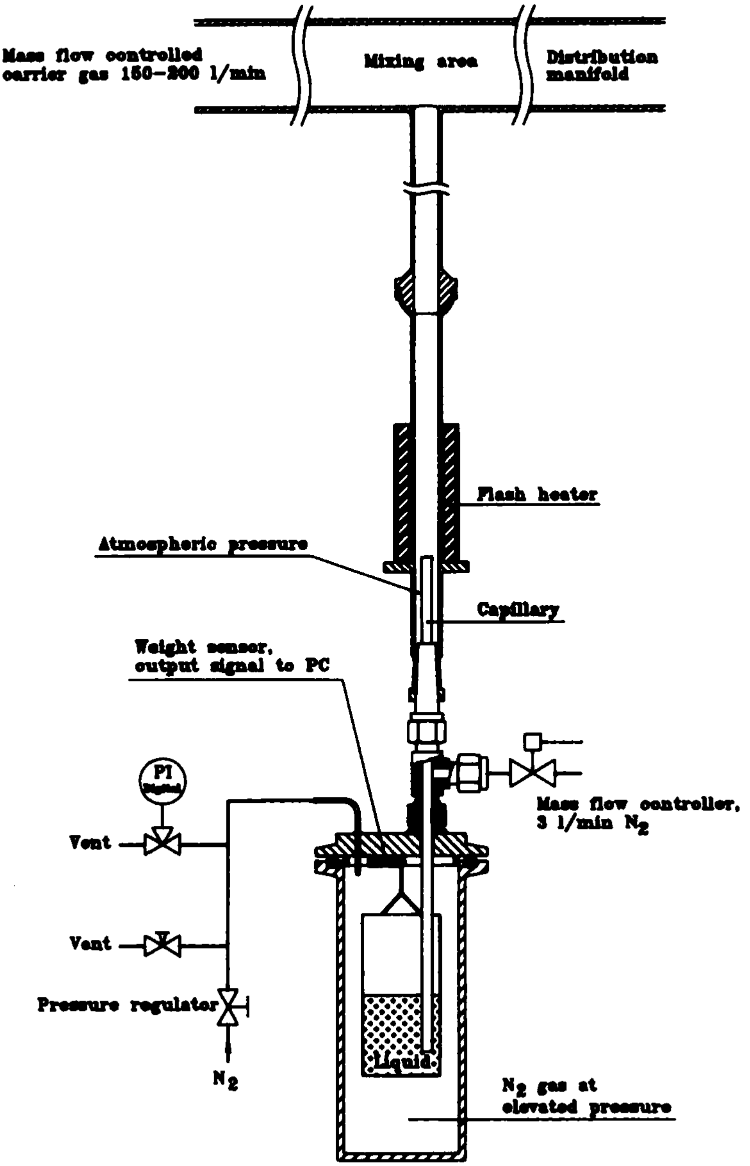

Figure 1 Scheme of the generation system for gaseous VOC's.

Four capillary dosage units are each equipped with one weight sensor. The weight sensors are made resistant towards the VOC vapours and an elevated pressure has no influence on their millivolt output signal. The output signal is calibrated by using a set of standard weights. Four weight sensors with three different operating ranges are installed: 0–10 g, 0–50 g, 0–150 g. The precision of the weight sensors is ±1%.

Principle of operation

The technique of capillary dosage is theoretically based on Poiseuille's equation which allows the calculation of the laminar flow through a cylindrical tube with radius r. For a pressure difference Δp over a length l, the fluid flow is given by Eq. 1:

$$Qv = \Delta p \pi r^4 / 8Nl \tag{1}$$

with: Δp = pressure drop across a cylindrical tube (N/m^2); r = internal tube radius (m), l = tube length (m), N = dynamic viscosity (kg/ms), and Qv = fluid flow (m^3/s).

From Eq. 1, the theoretical concentration of the different compounds in the carrier gas can be calculated.

In practice, the quantity of pure liquid emitted through a specific capillary is determined at different pressure settings. One obtains thus curves (and regressions) of pressure versus amount of liquid introduced into the diluent gas. These curves are specific for a typical capillary and a well-known chemical compound.

For these tests, the reservoir of the unit is filled with liquid. The reservoir is then connected with the weight sensor and the pressure is set at the appropriate value. The evaporated liquid is flash heated and carried to the manifold by a constant nitrogen flow of 3 l/min (mas-flow controlled). The amount of liquid injected into the carrier gas is measured on-line during the actual injection by a weight sensor connected to the data acquisition PC.

Performance characteristics

The performance of home-made capillary dosage units with in situ weight sensor is studied by distributing the spiked carrier gas through a glass manifold. The internal diameter of 40 mm is chosen to restrict the pressure difference across the entire length (46 m) of the manifold, hereby offering the possibility of sampling at atmospheric conditions even with high gas flow rates through the distribution manifold: 180–220 l/min at standard conditions (max. 250 l/min). Along the manifold a GC-FID with automatic sample loop continuously checks the actual concentration of the pollutants in the carrier gas and thus the stability of their concentration.

The performance of the units was evaluated for some aromatic hydrocarbons and chlorinated hydrocarbons. The use of the capillary dosage technique is not limited to these compounds. The pollutants to be charged should be liquid (pure or in solution) at the operating temperature. Testing the devices for all the VOC's seemed more or less senseless because the liquid or vapour comes only in contact with glass and PTFE sealings (which can be altered if necessary).

A very broad concentration range (ppm and ppb level) is obtained by using the available equipment. Table 1 shows some examples of possible concentrations. The levels for the compounds under test are focussed around the TLV-TWA limits[7] (0.2 to 2 times the TLV limit).

Table 2 shows that the amounts of liquid introduced are sufficient to detect gravimetrically by using a miniature weight sensor. The vessel containing the liquid should be made of an appropriate material and be as light as possible.

Table 1 Illustration of concentrations feasable using the gas generation unit and distribution system. Theoretical concentrations derived from Eq. 1.

*Compound**	*Capillary diameter (μm)***	*Pressure difference across capillary (bar relative)*	*Calculated theoretical release (μg/min)*	*Concentration in a total flow of 180 l/min (ppm)†*
Benzene	20	0.200	28.878	0.050
Benzene	20	3.000	433.163	0.744
Benzene	55	1.560	12882.054	22.2
Toluene	90	2.100	135526.7	198.1
Toluene	15	0.200	9.959	0.015
m-xylene	70	1.500	33594.9	42.5
Trichloroethene	55	2.505	38507.1	39.3

* The dynamic viscosity is the only variable in Eq. 1 which alters when using other VOC's.

** Length: 0.22 m.

† Flow at 294.15 K and 1013 hPa.

The in situ gravimetric determination of the concentration takes 3 to 5 hours for a majority of the concentration levels required for synthetic workplace air. More time is needed for the ppb level determinations. For long-time gravimetric determinations with low amounts of liquid injected, a correction has to be applied in order to figure out the amount of liquid evaporated in the stainless-steel housing (amount measured by the weight sensor and not introduced in the carrier gas).

The gravimetric determination of the weight loss of a compound during its injection process has a relative standard deviation over three experiments of ±1% (see Table 3).

These gravimetric experiments are performed for each capillary at different pressures using a pure liquid and thus result in calibration curves. These curves are essential for choosing the settings of a capillary dosage unit required in order to obtain the desired concentration. Figure 2 shows some curves.

Stability and homogeneity of gaseous VOC concentrations

An on-line analytical gas chromatograph monitors the VOC concentration in the distribution manifold. The gas chromatograph's sampling point is located approx-

Table 2 Released amounts of liquid by capillary dosage as function of elapsed time

Compound	*Concentration (ppm)*	*Liquid consumption (gram)*		
		after 3 h	*after 9 h*	*after 25 h*
Benzene	0.050	0.005	0.016	0.043
Benzene	0.744	0.078	0.234	0.650
Benzene	22.2	2.32	6.96	19.32
Toluene	198.1	24.40	73.18	—
m-Xylene	42.5	6.05	18.14	50.39
Trichloroethene	39.3	6.93	20.79	57.76

Table 3 Gravimetric determination of the liquid release of a capillary dosage unit determined by the in situ weight sensor

Parameter	*Compound*			
	Toluene	*Toluene*	*m-Xylene*	*Trichloroethene*
Capillary diameter (µm)	70	55	88	70
Pressure difference across the capillary (*10E5 Pa) (a)	0.510	1.896	1.240	1.000
Gravimetric determination of the liquid release (µg/min)	10138–10181 10288–10029	15243–15143 15281	93194–92700 93747	20744–20596 20694
Mean value of independent determinations	10159 ± 107	15222 ± 71	93124 ± 524	20678 ± 75
Percent rel. st. der.	1.1%	0.5%	0.6%	0.4%

[a] Pressure relative to atmospheric pressure.

imately in the middle of the distribution manifold. The gaseous sample is injected by a 250 µl sample loop into a wide-bore column and detected by an FID. Figure 3 and Figure 4 show the stability data expressed as peak area in function of the elapsed time.

To demonstrate the homogeneity of the test gas, samples were taken at different locations along the manifold. These tests indicate no increase in the relative standard deviations. The installation is therefore suitable for the organisation of intercomparison exercises.

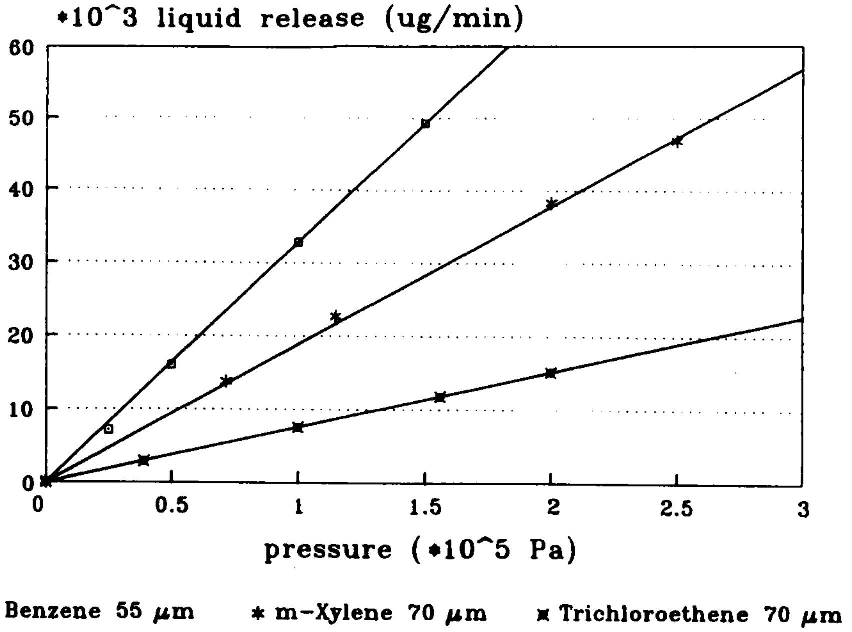

Figure 2 Calibration curve for various VOC compounds using glass capillaries with a diameter of 55 µm and 70 µm.

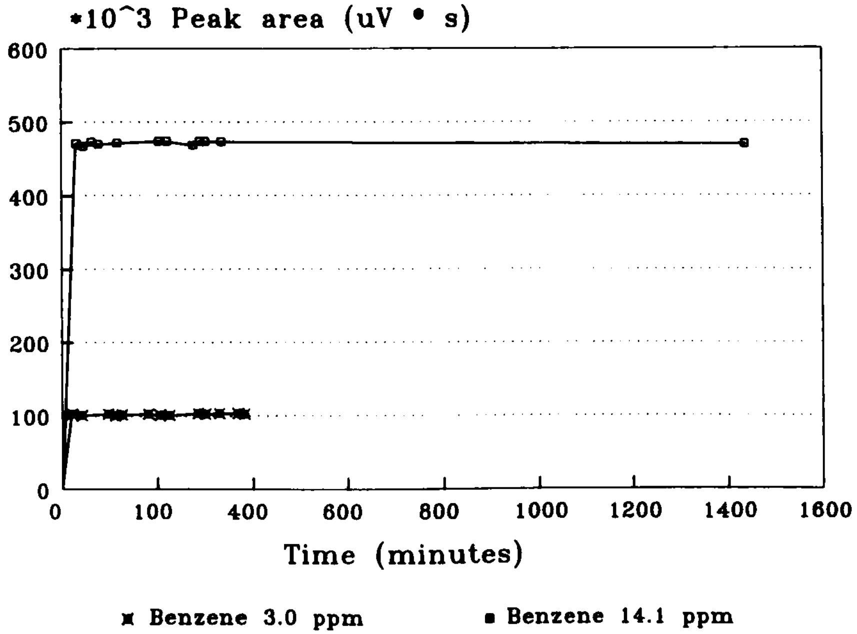

Figure 3 Stability of the gaseous benzene concentration. Series 1: mean peak area, 101607 μV.s; RSD, 1.07%. Series 2: mean peak area, 471176 μV.s; RSD, 0.10%.

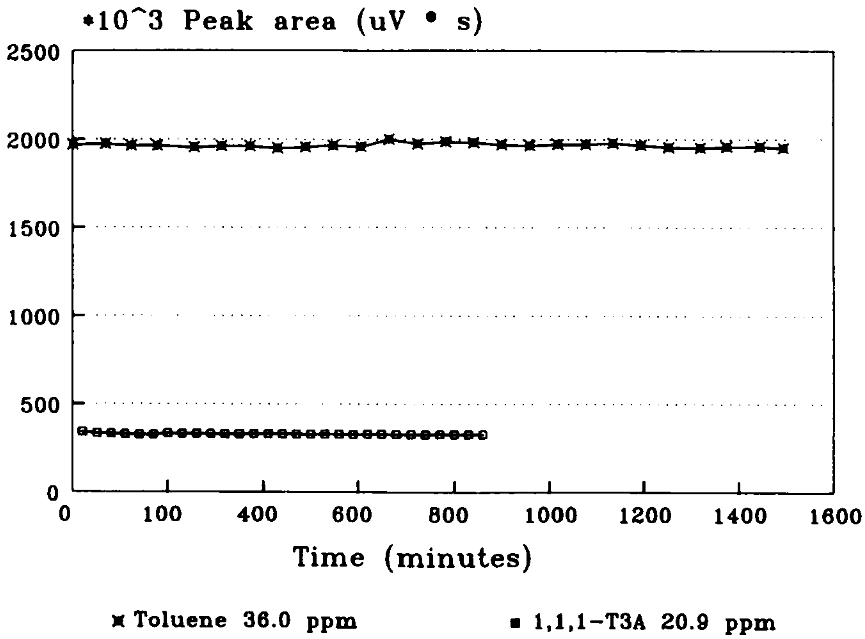

Figure 4 Stability of the gaseous toluene and trichloroethane concentration. Series 1: mean peak area, 1964600 μV.s; RSD, 0.60%. Series 2: mean peak area, 328609 μV.s; RSD, 0.10%.

Independent control of the standard VOC concentrations in the manifold

The uncertainty of a standard VOC concentration generated from a capillary dosage device depends not only on the performance of this device but is also determined by the accuracy of flow control and measurement. The carrier gas is mass-flow controlled and thus extremely stable. The uncertainty of an indicated VOC concentration is assessed as follows:

—uncertainty of flow measurements: ≤1%

—stability and repeatability of a mass flow controlled flow: 0.3%

—gravimetric determination of a compounds' weight loss during injection: ≤1%

—reproducability of a pressure setting: ≤1%.

The overall uncertainty is thus estimated at 2–3%.

Capillary dosage versus diffusion tubes

The diffusion tube method according to ISO 6145 is applied in order to detect possible errors in the gravimetric measurements as used in the capillary dosage device. The on-line analytical gas chromatograph is primary calibrated by means of diffusion tubes. In this way, the AGC provides an additional control of the prepared standard concentrations.

Table 4 Capillary dosage versus diffusion tubes

Compound	*Concentration as calculated from weight measurements (ppm)*	*Concentration measured by GC using diffusion tubes for calibration (ppm)*
Benzene	11.7 ± 0.5	11.8 ± 0.5
Toluene	15.0 ± 0.5	15.1 ± 0.5
Toluene	92 ± 2	93 ± 2
m-Xylene	17.3 ± 0.5	17.1 ± 0.5
m-Xylene	43 ± 2	42 ± 2
m-Xylene	106 ± 3	103 ± 3

Capillary dosage versus calculated theoretical concentration

Equation 1 is used to determine the calculated theoretical concentration. All variables are well-known, only the diameter of the capillary should be determined as accurately as possible. The capillary is cut into a number of disks and the mean diameter is determined by microscopy.

This comparison between theoretical and empirical values of the gaseous VOC concentration is done only to show the agreement. It is not useful in practice since the capillary diameter is determined in a destructive way so that the capillary cannot be used anymore in the capillary dosage device. Therefore the comparison is only accomplished for a few compounds and concentrations.

Table 5 Capillary dosage versus calculated theoretical concentration

Compound	*Capillary diameter (μm)*	*Pressure difference across capillary (bar relative)*	*Theoretical concn. (ppm)*	*Real concn. (ppm)*
Benzene	54 ± 1	0.900	13.9 ± 1.0	14.1 ± 0.5
Toluene	88 ± 1	1.000	101 ± 4	104 ± 3
m-Xylene	69 ± 1	0.600	18.9 ± 1.1	17.3 ± 0.6

CONCLUSIONS

A capillary dosage unit emits a pollutant at a constant rate when the pressure difference across the capillary remains constant. The rate of pollutant emitted is determined during the injection process or previous to this in gravimetric experiments. This is a major advantage as compared to other currently used techniques. Temperature fluctuations influences the viscosity of the liquid in the capillary dosage device and should only be taken into account for calculations of the concentration according to Eq. 1.

Frequent measurements of the diluent gas flow are not required. In the capillary dosage technique, the diluent gas flow remains the same. A range of standard concentrations for calibration purposes are obtained by varying the pressure difference across the glass capillary and measuring accurately the weight loss of the pollutant during its injection.

It is clear from the experiments that an in situ weight sensor allows to measure the amount of pollutant emitted into a carrier gas very accurately and this during the injection process without interfering with it. By using a set of capillary dosage devices one is able to prepare ppb and ppm levels of standard gaseous VOC concentrations in the same diluent gas flow. The nominal gas flow through the sampling manifold is 180 l/min at standard conditions.

The described experimental facility offers new possibilities regarding: (i) the organisation of intercomparisons for workplace air sampling and analysis (up to 150 l/min gas available for active sampling); (ii) research and development of analytical methodology for sampling and analysis of workplace air; (iii) study of interference, precision and accuracy of personal samplers; (iv) active sampling versus passive sampling.

References

1. A. E. Keeffe and G. C. Ortman, *Anal. Chem.* **38**, 760–763 (1966).
2. O. Keeffe and G. C. Ortman, *Anal. Chem.* **39**, 1047–1048 (1967).
3. Preparation of calibration gas mixtures—permeating method, ISO 6349.
4. Preparation of calibration gas mixtures—dynamic volumetric methods, diffusion, ISO 6145—part 8.
5. A. P. Altshuller and I. R. Cohen, *Anal. Chem.* **32**, 802–810 (1960).
6. Preparation of calibration gas mixtures—dynamic volumetric methods, continuous injection method, ISO 6145—part 4.
7. TLV values, Commissariaat-Generaal voor bevordering van de arbeid (1985), Brussels, Belgium.