



The controlling effect of temperature in the application of permeation tube devices in standard gas generation

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ABSTRACT

In this study, the performance of permeation tube (PT) devices for the generation of VOC calibration gas was examined by successively generating BTX gas at five temperatures (30, 50, 70, 80, and 100 °C) and two flow rates (400 and 800 mL min⁻¹). A distinct relationship was observed between temperatures and permeation rates (PR) (or generated BTX concentrations). We examined the reliability of the manufacturer's PR formula when operating at chamber temperatures different from the manufacturer reference temperatures for each PT device. Bias of the actual PR from the theoretical PR values became significant as PT devices were operated at temperatures beyond their optimum operating range (e.g., maximum bias of BTX as 141%, 87.2%, and 85%, respectively). Through a derivation of empirical formula, we were able to predict PR values of the target compounds more accurately as evidenced by significant bias reduction at all temperature points (e.g., maximum bias of BTX as 10.9%, 21.1% and 20.6%, respectively).

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1. Introduction

Teflon permeation tube (PT) devices have been an effective source of gas standards for instrument calibration in atmospheric trace gas measurements [1]. A PT device is a small permeable tube filled with a pure chemical compound to induce a two-phase equilibrium between the gas and liquid (or solid) phase. At a given temperature, the PT device dispenses a miniscule amount of the permeative vapor at a constant rate through the gas permeable walls of the PT. Most PT are constructed of polymeric membranes typically made of tetrafluoroethylene (TFE) or fluorinated ethylene propylene (FEP: Teflon®). PT has been proven effective for creating low concentration gas mixtures in parts per million (ppm) to parts per trillion (ppt) ranges with high precision and accuracy ($\pm 1\%$) [2,3]. Their permeation rates are established by a gravimetric weight loss method after equilibration at a specified temperature [3]. For a stable compound, its permeation rate (PR) is extremely steady as long as liquid remains visible in the PT device [1].

Currently, over 400 compounds are commercially available as NIST traceable gas standards, and this PT technology has been used towards various applications [1]. Since the early recognition on its wide applicability for standard gas preparation, interest in this

product has steadily been increasing, especially with the growth in air quality research and regulation [4–6]. Manufacturers also claim that the PT is capable of generating NIST traceable, accurate, and repeatable gas standards over a long term period. Although the use of compressed gas cylinders is still believed to be the most reliable and stable tool for standard gas calibration, the use of PT has several advantages of its own such as low cost, light weight, and small space requirements [7–11]. Generation of gas standards from PT devices is usually done with the aid of a calibration gas generator equipped with a temperature controlling unit. With the accurate control of temperature and gas flow rate (FR), one can produce a known quantity of mixture at a constant permeation rate (PR) at a given FR.

In an earlier study, we observed that estimating PR using the manufacturer's given formula can result in a large bias that greatly depends on diluent gas supply rate [12]. In general, operating temperature of PT device is recommended in the range of 30–110 °C to maintain PR reliably [1]. Knowing that the temperature is one of the key variables which can sensitively affect the generation of PT standard, its effect on the PT performance was further investigated in this study with the aid of a constant temperature gas standard generator system. To this end, we measured actual PR (APR) values of BTX with temperatures varying from 30 to 100 °C and explored the level of experimental bias stemming from theoretically predictable manufacturer's PR (MPR) values. Based on this comparative analysis, we further developed equations for predicted

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Table 1
Basic information and permeation tube information for three target compounds used in the experiment.

Compound full name	Benzene	Toluene	m-Xylene
Abbreviation	B	T	m-X
Molecular formula	C ₆ H ₆	C ₇ H ₈	C ₈ H ₁₀
Density (g cm ⁻³)	0.88	0.87	0.86
MW (g mol ⁻¹)	78.11	92.14	106.2
CAS no.	71-43-2	108-88-3	108-38-3
Sales order no.	102597	102597	102597
Part no.	100-160-1400-U70	100-183-1401-U80	100-114-1403-U100
Type	HE ^a	HE	HE
Total length (cm)	19.5	21.8	14.9
Diameter (cm)	0.98	0.98	0.98
Reference permeation rate (PR ₀) at reference temperature (T ₀) ^b			
PR ₀ (ng min ⁻¹)	16,000 ± 15%	18,849 ± 15%	21,774 ± 15%
T ₀ (°C)	70	80	100
Molar constant (K) over a range of temperature ^c			
T = 30 °C	0.32	0.27	0.23
T = 50 °C	0.34	0.29	0.25
T = 70 °C	0.36	0.31	0.27
T = 80 °C	0.37	0.31	0.27
T = 100 °C	0.39	0.33	0.29
Manufacturer's permeation rate (MPR in ng min ⁻¹) of PT devices due to the temperature change ^b			
T = 30 °C	698	376	90.8
T = 50 °C	3343	1800	434
T = 70 °C	16000	8616	2079
T = 80 °C	35004	18849	4549
T = 100 °C	167541	90217	21774

^a HE implies that the device is built for high emission rate.

^b If a permeation rate (P₀) is known at some reference temperature (T₀), a new permeation rate (P₁) at a different temperature (T₁) can be estimated according to the manufacturer's formula as follows: $\log P_1 = \log P_0 + 0.034(T_1 - T_0)$.

^c Molar constant (K) = R·T/MW; where R = gas constant 0.082057 L atm/mol K; T = absolute temperature (°K); and MW = molecular weight (g mol⁻¹). K is included in the manufacturer's equation to calculate concentration (refer to Eq. (2)).

permeation rate (PPR) to replace the MPR equations across a range of temperature. This effort will ultimately help us further overcome the basic experimental biases involved in PT application.

2. Methods

2.1. PT device and dynacalibrator system

Dynacal PT devices with Teflon tubes were purchased from Valco Instruments Co. Inc. (VICI Metronics Inc., USA). The PTs had manufacturer-specified reference PR of 16,000 ng min⁻¹ (at 70 °C optimum operating temperature) for benzene (B), 18,849 ng min⁻¹ (at 80 °C) for toluene (T), and 21,774 ng min⁻¹ (at 100 °C) for m-xylene (X). Basic information on the target compounds (e.g., structural formula, density, molecular weight, and CAS no.) and PT device (e.g., sales order no., part no., type, and PR at a certain temperature) are presented in Table 1.

The portable calibration gas generator with temperature controlling system (Dynacalibrator Model 150, VICI Metronics, Inc.) was employed to generate chemical compounds across a varying temperature range (Fig. 1). The dynacalibrator features a glass-coated stainless steel permeation chamber and cap which houses one or more permeation devices. The permeation chamber is passivated with an Inertium and Ultradeactivation coating. The passivated glass coating of the stainless steel chamber assembly is compatible with most chemicals (including sulfur compounds) except hydrofluoric acid [1]. The temperature of the chamber which directly affects the permeation (or diffusion) rate of the trace gas can be controlled digitally in the range of 30–110 °C (accuracy ±0.01 °C), traceable to NIST standards. This wide range of temperature settings allows one to use the PT devices with compounds covering a relatively wide vapor pressure range.

Moreover, manufacturers recommend a carrier gas (which sweeps the calibration gas/vapor from the chamber of the dynacalibrator) flow range from 100 to 1200 mL min⁻¹. Hence, the desired volumetric concentration is changed by simply varying the inert carrier gas flow or the operating temperature.

2.2. Generation of standard gas by PT

The PT devices for BTX were wiped clean and placed inside the permeation chamber of the dynacalibrator using forceps (Fig. 1). In order to generate the desired concentration of the three compounds, the permeation chamber was supplied steadily with an inert carrier gas (ultrapure N₂). In this study, we generated BTX concentrations at five temperatures (30–100 °C) and two intermediate flow rates (800 and 400 mL min⁻¹) (Table 1). As it is more convenient to raise temperature of dynacalibrator oven, the experiment was initiated at the lowest temperature of 30 °C and proceeded to the next levels. To maintain the diffusion of standard gas mixtures at a constant level, one needs to establish stabilization of the operating temperature [13]. Thus, we ensured to collect gas mixtures during stabilized period of the dynacalibrator system when chamber temperature has been within 0.1 °C of the set point temperature value (indicated by a solid green light of the temperature button). In our experiment, it generally took from 90 to 105 min to reach re-equilibrium at the next level of temperature set for the experiment.

Upon supply at the inlet of the dynacalibrator, N₂ gas sweeps the calibration gas/vapor from the chamber (Fig. 2a). An initial short flushing time was given prior to each run to saturate the permeation chamber with the desired concentration of the three target compounds. Flow rate was measured at the outlet after every flow rate change and prior to sampling. Pressure gauges were installed at the inlet and outlet flow lines of the dynacalibrator to monitor the

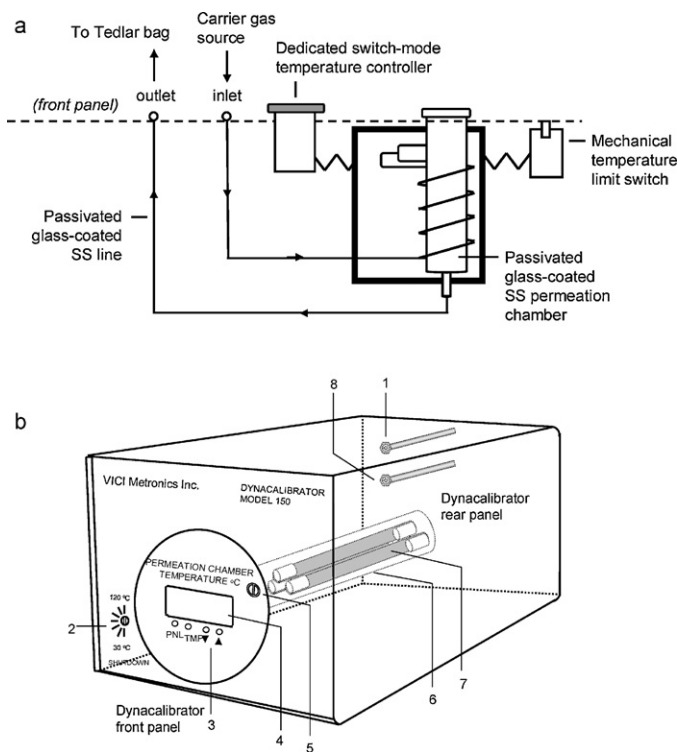


Fig. 1. Calibration gas generation system (Dynacalibrator Model 150): (a) schematic (source VICI Metronics Dynacalibrator Model 150 Instruction Manual) and (b) internal and external parts of the instrument (not detailed). Labels: 1, carrier source inlet; 2, chamber temperature limit switch; 3, digital temperature controller; 4, temperature display; 5, panel lock; 6, permeation chamber; 7, permeation tube device; and 8, outlet.

difference in pressures between the two ports (Fig. 2a). The pressure build-up at the inlet port was measured at 1275 and 686 hPa at 800 and 400 mL min⁻¹, respectively. However, there was no pressure build up at the outbound flow line. Because the PT chamber can be contaminated under the absence of carrier flow [14], the carrier flow was supplied simultaneously with the placement of PT devices inside the dynacalibrator.

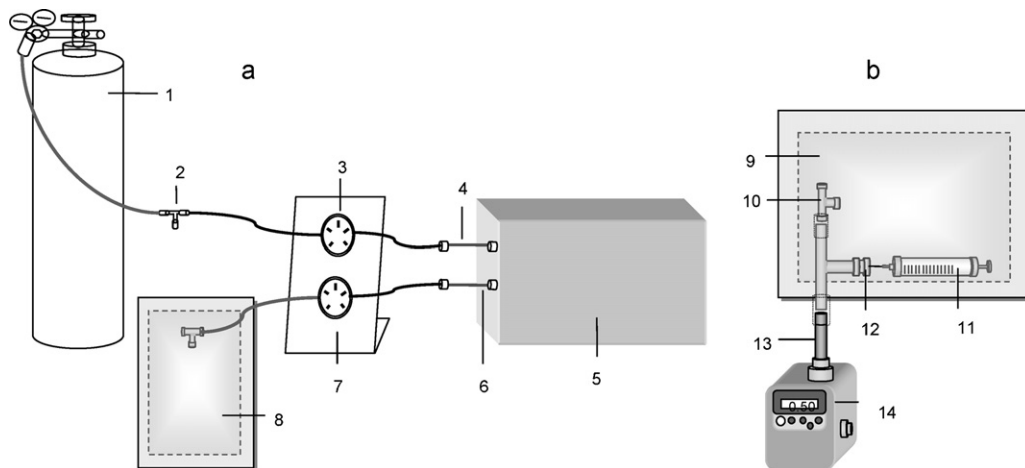


Fig. 2. Illustration of the validation procedure for the BTX gas generated from PT devices. (a) Production of permeant gas: N₂ from cylinder tank is supplied as diluent for the PT devices contained inside dynacalibrator device so that the initially empty Tedlar bag (left) is filled with the permeant gas. (b) Collection of permeant gas by sorbent tube for GC analysis: the gaseous analytes produced and stored in Tedlar bag (left) is withdrawn and injected into the sorbent tube using a gas-tight syringe with the constant supply of back-up gas from another Tedlar bag (right) filled with N₂. Labels: 1, pure N₂ tank; 2, N₂ flow regulator; 3, inlet pressure gauge; 4, dynacalibrator inlet; 5, Dynacalibrator Model 150 by VICI Metronics Inc. (containing permeation tube devices); 6, dynacalibrator outlet port; 7, outlet pressure gauge; 8, initially empty 10L Tedlar bag (to contain collected permeates of B, T, and X); 9, Tedlar bag containing N₂ gas; 10, Tedlar bag injection port; 11, gas-tight syringe containing the target analytes; 12, temporary injection port; 13, sampling sorbent tube with carbopack-X; and 14, Sibata pump (set at 0.2 L min⁻¹ for a total of 1 L).

The compounds which permeated from the PT device were mixed by the diluent gas flow, and the mixture was initially captured in an empty 10 L polyvinyl fluoride (Tedlar®) bag (Fig. 2a). All Tedlar bags were flushed with ultra-pure N₂ several times prior to use and subjected to bag blank analysis. After filling, the Tedlar bags were stored at room temperature in the dark and BTX concentrations were analyzed within 24 h using the tube sampling method.

A second Tedlar bag containing ultra-pure N₂ (also used as carrier gas) was attached to the inlet of the stainless steel sorbent tube (containing 300 mg of carbopack-X as sorbent material) via a temporary injection port (Fig. 2b). A minipump (Sibata, Japan) was then attached at the outlet of the sorbent tube. All sorbent tubes were thoroughly conditioned to remove possible trace BTX contamination before use. The minipump settings were adjusted to transfer N₂ contained inside the Tedlar bag to the sorbent tube at a mean FR of 0.2 L min⁻¹ for the duration of 5 min. Transfer of target analytes into the sorbent tube was made while the N₂-flushing gas flowed toward the sorbent tube (Fig. 2b) as follows: 10 mL of each sample was slowly withdrawn from the Tedlar bag containing the gas standard (Fig. 2a) by gas-tight syringe and injected into sorbent tubes via a temporary injection port. As samples taken at higher temperatures (e.g., 100 °C) have significantly higher concentrations (e.g., 209 ng mL⁻¹ of B), we added one-step dilution to achieve a target analyte concentration within the normal quantification range for the GC.

2.3. Cylinder gas standard calibration and GC-FID analysis

The sorbent tubes loaded with the PT-generated BTX gas were analyzed using an Ultra/Unity-TD autosampler (Markes International, UK) and GC-FID system (Varian 450-GC, USA). The instrument settings are shown in detail in Table 2. Method detection limits were calculated for all target compounds prior to the experiment. The detection limits for B, T, and X were 0.36, 0.72, and 0.22 ppb (or 1.2, 2.7, and 0.8 ng in absolute mass), respectively. Gas-based calibrations were also conducted before each experiment set using 6 ppm standard of BTX. The mixture of this 6 ppm BTX was prepared by injecting 300 mL of 20 ppm BTX standard from a compressed gas cylinder (Rigas, Dae Jeon, South Korea) (using a gas-tight syringe) into a 1-L Tedlar bag filled partially with 700 mL of ultra-pure N₂. The standard mixture was then allowed to

Table 2
TD and GC-FID settings for the analysis of PT-generated standards of BTX by sorbent tube method.

GC-FID system (Varian 450-GC, USA)		Detector setting	
Column: CP-WAX 52CB (length: 60 m, ID: 0.25 mm, film thickness: 0.25 μm , Chrompack)			
Oven setting		Detector setting	
Oven temp.	50 °C (5 min)	Detector temp.	240 °C
Oven ramp rate	6 °C min ⁻¹	H ₂ flow	30 mL min ⁻¹
Max oven temp.	230 °C (5 min)	N ₂ flow	29 mL min ⁻¹
Total time	40 min	Air flow	30 mL min ⁻¹
Thermal desorber (Unity, Markes, UK)			
Sorbent tube/sample desorption temp.	300 °C	Valve temp.	120 °C
Sorbent tube/sample desorption time	10 min	Transfer line temp.	120 °C
Cold trap temp (low)	5 °C	Minimum pressure	10 psi
Cold trap temp (high)	300 °C	Split ratio	0
Cold trap hold time	5 min		

stand for 15 min for stabilization and transferred to sorbent tubes as described previously [6]. The procedure involved the injection of the required amount of the BTX standard to the stream of carrier gas flowing towards the sorbent tube (Fig. 2b). Concentration ranges of the injected BTX standard are listed in Table A.1. The concentrations of target compounds in the PT-generated standard were computed by calibration slopes obtained from the cylinder gas standards (refer to Table A.1). Linearity of the system was excellent with R^2 values greater than 0.98 for all three compounds (Table A.1). Precision, if expressed in terms of relative standard error (RSE) values, was excellent at 0.14%, 0.46%, and 1.21% for BTX, respectively (Table A.1).

2.4. Temperature-based PR adjustment and calculation of generated gas standard concentrations

The PR values are initially given by the manufacturer for each target compound at a respective reference temperature (Table 1). The PR values at other temperature settings can be approximated using Eq. (1) (VICI Metronics Dynacalibrator Model 150 Instruction Manual) [1].

$$\log \text{MPR} = \log \text{PR}_0 + 0.034(T - T_0) \quad (1)$$

where PR_0 = permeation rate at a reference temperature (T_0) and MPR = permeation rate at adjusted temperature (T).

Eq. (1) is reported to be valid in the temperature range of 30–110 °C [1]. These MPR values and the corresponding manufacturer's concentration (MC) values are listed in Table 1. The MC term can be derived by the following general formula for concentration (C):

$$C = \frac{(\text{PR} \times K)}{F} \quad (2)$$

where C = gas standard concentration in ppm; PR = permeation rate (ng min^{-1}); K = molar constant ($RT/\text{molecular weight of gas}$); and F = diluent flow rate (mL min^{-1}). The concentrations of these PT-generated gases, initially collected in Tedlar bags, were quantified by the sorbent tube method described above against the reference standard from the compressed gas cylinder. These measured concentrations of BTX were then defined as the actual measured concentrations (AC) and used to derive the corresponding actual permeation rate (APR) values.

2.5. Quality assurance/control (QA/QC) measures

Temperature control for stable operating conditions is crucial to generate calibration gas from a PT device at the desired concentration [15]. McKinley [14] reported that the emission rate from a liquid fed PT device typically varies about 10% per 1 °C change. Hence, a control of ± 0.1 °C assures emission accuracy within $\pm 1\%$. The dynacalibrator is reported to show the accuracy of ± 0.01 °C

at constant chamber temperature ranging from 30 to 110 °C [1]. Hence, permeation rate of compounds released from the PT devices is expected to be highly stable and constant.

A number of factors (e.g., the supply rate of the carrier gas, the extent of back diffusion, and accuracy of FR control) are suspected as the main sources of error in the PT operation (e.g., [15]). It is important to check the bias induced by such factors, as the 2nd phase of the experiment (calibration of the PT-generated gas mixture) was conducted by a controlled addition of the BTX gas mixture to the moving stream of carrier gas (N₂ supplied at 200 mL min⁻¹) toward the sorbent tube (Fig. 2b). In this experiment step, error was reduced fairly effectively as evidenced by the highly reproducible results with RSE in the range from 0.03% to 1.21% for BTX with good calibration linearity (R^2 values >0.98 for BTX).

3. Results and discussion

3.1. The effect of temperature change on AC and APR of PT-generated gases

Table 3 presents the actual concentration data of the PT-generated standard gas measured across varying temperatures and flow rates for each compound. It should be noted that these actual PT-generated concentration (AC) data sets were also used to derive the actual permeation rate (APR) values. Hence, temperature effect on AC was examined simultaneously with that of APR.

To examine the effect of temperature on the observed performance of PT, both AC and APR values of BTX were plotted against temperature (Figs. 3 and 4). AC increased systematically with increases in temperature throughout all experiments. Similar trends have been reported in previous studies [16,17]. Coefficient of determination (R^2) derived from the relationship between temperature and APR were >0.99 at both FR (Fig. 3). Other researchers have observed exponential increases in the permeability of Teflon with temperature, which has been described as a swelling phenomenon. Thus, diffusion rates of PT should be strongly dependent on temperature, in addition to the properties of the membrane material and its dimensions [16,18].

Permeation rate was reported to be continuous and stable at equilibrium conditions, while being directly dependent on temperature control [3,13,19]. In this experiment, the stability of each operating temperature setup on the dynacalibrator was found to be highly consistent as evidenced by the highly reproducible concentration data from triplicate analyses. The attainment of stable operating temperatures is evidenced by minimal relative standard error values (RSE in %) for all compounds across all temperatures and FR investigated (Table 3), with the maximum value at around 5.6% (observed with m-X at 30 °C and 400 mL min⁻¹ FR). Moreover, reproducibility was enhanced at intermediate temperatures (e.g., 50, 70, and 80 °C),

Table 3
Permeation rates of BTX in terms of three different definitions and the associated experimental bias.

Order	Compound	Diluent (N ₂) flow rate (mL min ⁻¹)	Operating temperature (°C)	Concentration (C) (ng mL ⁻¹)		Permeation rate (PR) (ng min ⁻¹)					Difference from APR (%) ^e				
				MC ^a	PC ^b	AC			Average	% RSE	MPR	APR ^c	PPR ^d	MPR	PPR
						R1	R2	R3							
1	Benzene	800	100	209	91.1	82.4	87.8	90.5	86.9	2.74	167,541	69,527	72,912	141	4.87
2			80	43.8	24.1	22.9	23.2	23.6	23.3	0.85	35,004	18,605	19,266	88.1	3.56
3			70	20.0	12.4	13.5	13.4	13.2	13.4	0.60	16,000	10,710	9904	49.4	7.53
4			50	4.18	3.27	3.68	3.66	3.68	3.67	0.17	3343	2938	2617	13.8	10.9
5			30	0.87	0.86	0.80	0.78	0.76	0.8	1.43	698	624	692	12.0	10.9
6		400	100	419	233	218	211	233	221	2.97	167,541	88,265	93,261	89.8	5.66
7			80	87.5	67.5	64.4	64.3	65.2	64.6	0.42	35,004	25,847	27,021	35.4	4.54
8			70	40.0	36.4	39.0	38.7	38.8	38.8	0.23	16,000	15,529	14,545	3.03	6.34
9			50	8.36	10.5	12.2	11.6	11.3	11.7	2.30	3343	4669	4214	28.4	9.74
10			30	1.75	3.05	2.83	2.70	2.76	2.76	1.38	698	1105	1221	36.8	10.5
11	Toluene	800	100	113	70.3	58.3	60.8	61.6	60.3	1.65	90,217	48,202	56,234	87.2	16.7
12			80	23.6	19.1	19.7	19.6	19.8	19.7	0.29	18,849	15,755	15,276	19.6	3.05
13			70	10.8	9.95	12.1	12.0	11.8	12.0	0.56	8616	9564	7962	9.92	16.8
14			50	2.25	2.70	3.19	3.16	3.18	3.17	0.28	1800	2538	2163	29.1	14.8
15			30	0.47	0.73	0.57	0.64	0.62	0.61	3.41	376	485	587	22.5	21.1
16		400	100	226	149	150	146	159	152	2.68	90,217	60,670	59,745	48.7	1.53
17			80	47.1	49.0	49.7	49.4	49.0	49.4	0.37	18,849	19,753	19,602	4.58	0.77
18			70	21.5	28.1	28.8	28.5	28.9	28.7	0.43	8616	11,497	11,228	25.1	2.34
19			50	4.50	9.2	7.97	8.05	7.94	7.98	0.40	1800	3194	3684	43.6	15.3
20			30	0.94	3.02	3.62	3.12	3.14	3.29	4.90	376	1317	1209	71.4	8.24
21	m-Xylene	800	100	27.2	24.9	20.3	20.8	20.8	20.6	0.86	21,774	16,502	19,907	31.9	20.6
22			80	5.69	6.92	7.27	7.18	7.21	7.22	0.39	4549	5775	5534	21.2	4.19
23			70	2.60	3.65	4.45	4.41	4.34	4.40	0.73	2079	3518	2917	40.9	17.1
24			50	0.54	1.01	1.13	1.13	1.13	1.13	0.06	434	903	811	51.9	10.2
25			30	0.11	0.28	0.22	0.24	0.24	0.24	2.45	90.8	188	225	51.8	19.7
26		400	100	54.4	49.4	49.9	49.1	52.7	50.5	2.17	21,774	20,217	17,989	7.70	11.0
27			80	11.4	16.1	16.2	16.2	16.1	16.2	0.21	4549	6463	6531	29.6	1.05
28			70	5.20	9.2	8.96	8.87	8.95	8.93	0.30	2079	3571	3936	41.8	10.2
29			50	1.09	3.01	3.22	3.11	2.95	3.09	2.54	434	1237	1429	64.9	15.5
30			30	0.23	0.98	1.52	1.66	1.37	1.51	5.60	90.8	606	519	85.0	14.3

MC = given concentration derived using manufacturer's equation; PC = predicted concentration derived using the permeation rate equation based on the actual measured data; AC = actual measured concentration of the PT-generated standard from our experiment; MPR = given permeation rate calculated based on the manufacturer's equation; PPR = predicted permeation rate derived from our experiment; and MPR = measured permeation rate.

^a Given concentration of each compound is calculated based on the manufacturer's permeation rate (ppm) = $K \times P/F$; where: P = permeation rate (ng min⁻¹); F = dilution flow (mL min⁻¹); K (compound molar constant in g L⁻¹) = $R \cdot T/MW$ (R = gas constant 0.082057 L atm/mol K; T = 273 + actual temperature; and MW = molecular weight of gas).

^b Equation for predicted concentration in ng mL⁻¹ (Y) for each compound was derived using linear regression with temperature (°C) as independent variable X . At 800 mL min⁻¹: $Y_{\text{benzene}} = 10^{0.0289x-1.9303}$; $Y_{\text{toluene}} = 10^{0.0283x-0.9831}$; $Y_{\text{m-xylene}} = 10^{0.0278x-1.3841}$. At 400 mL min⁻¹: $Y_{\text{benzene}} = 10^{0.0269x-0.3224}$; $Y_{\text{toluene}} = 10^{0.0242x-0.2458}$; $Y_{\text{m-xylene}} = 10^{0.0220x-0.5171}$.

^c Equation for actual measured permeation rate (APR in ng min⁻¹) = $C \times F/K$ where C = measured concentration in ng mL⁻¹; F = flow rate in mL min⁻¹; and K = compound molar constant in g L⁻¹.

^d Equation for predicted permeation rate in ng min⁻¹ (Y) for each compound was derived using linear regression with temperature (°C) as independent variable X . At 800 mL min⁻¹: $Y_{\text{benzene}} = 10^{0.0289x+1.9728}$; $Y_{\text{toluene}} = 10^{0.0283x+1.9200}$; $Y_{\text{m-xylene}} = 10^{0.0278x+1.519}$. At 400 mL min⁻¹: $Y_{\text{benzene}} = 10^{0.0269x+2.2797}$; $Y_{\text{toluene}} = 10^{0.0242x+2.3563}$; and $Y_{\text{m-xylene}} = 10^{0.0220x+2.055}$.

^e Absolute difference (%) = $((\text{MPR (or PPR)} - \text{APR})/\text{APR}) \times 100$.

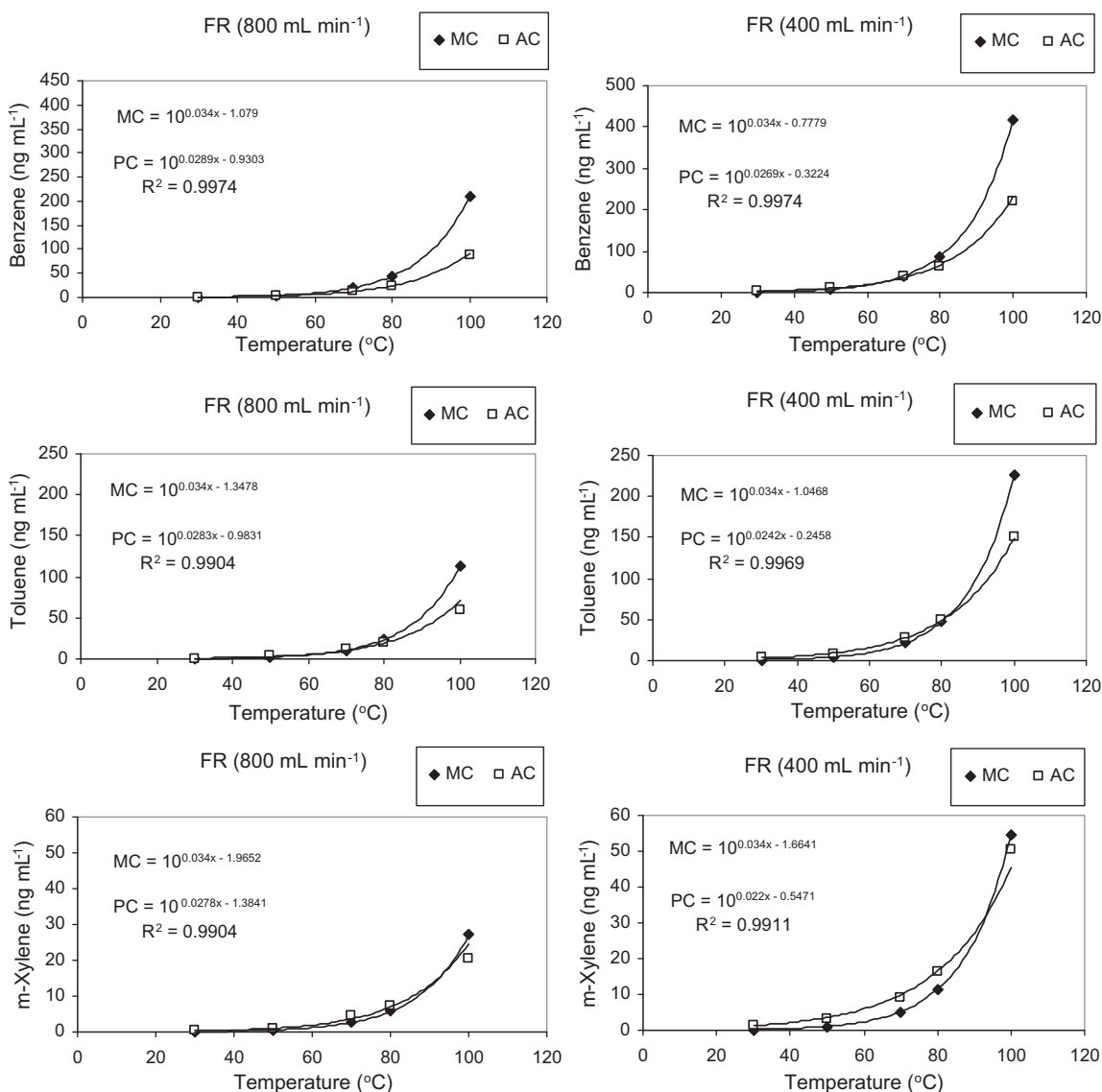


Fig. 3. Relationship between the measured concentration (ng mL⁻¹) of BTX and temperature (°C). Labels: MC, manufacturer's given concentration; AC, actual measured concentration; and PC, predicted concentration.

although the RSE values tend to rise at the extreme settings (e.g., 30 and 100 °C).

3.2. Comparison between APR and MPR (or AC and MC) values

The actual measured concentration (AC) values of BTX were compared with those expected concentrations based on the manufacturer's given equations (MC) at each specific temperature. To this end, MPR and APR were plotted against temperature to check their compatibility. The differences between MPR from APR derived in terms of % difference values are also plotted in Fig. 5a and b.

Although the manufacturer of the dynacalibrator system claimed reliability of standard gas generation (even for multi-component mixture) at temperatures ranging from 30 to 110 °C, our results suggests that MPR were only reliable when the PT device was operated at or near its optimum temperature given by the manufacturer. Here, optimum operating temperature for individual PT device can be defined as the most favorable temperature setup suggested (by the manufacturer) to gain the most reliability. It was recognized that the MPR values at FR of 400 mL min⁻¹

reached the highest compatibility at their optimum operating temperatures. This is illustrated by the least difference between APR and MPR (3.03% (B), 4.58% (T), and 7.70% (X)) at their respective optimum temperature points 70, 80, and 100 °C (Table 3; Fig. 5b). Moreover, the bias between APR and MPR increased as the operating temperature deviated from the recommended temperature.

According to the collected evidence, the use of the reference temperature can be considered one of the critical factors for PT application, especially if their performance cannot be examined by other means [12]. Our study further suggests that end users should be careful when using the manufacturer-given equations to predict PR. This bias can be more significant, if PT devices are used below or above their optimum operating temperatures.

There was a distinct relationship between temperature and flow rate, when the permeation rate of a given compound was examined in relation to such variables. The PR ratio for a given gas, if compared between the highest temperature (100 °C) and the lowest temperature (30 °C), was consistently higher at 800 than 400 mL min⁻¹ (Table 3). In contrast, the actual PR value at the lowest temperature (30 °C) was consistently higher at 400 than 800 mL min⁻¹. As

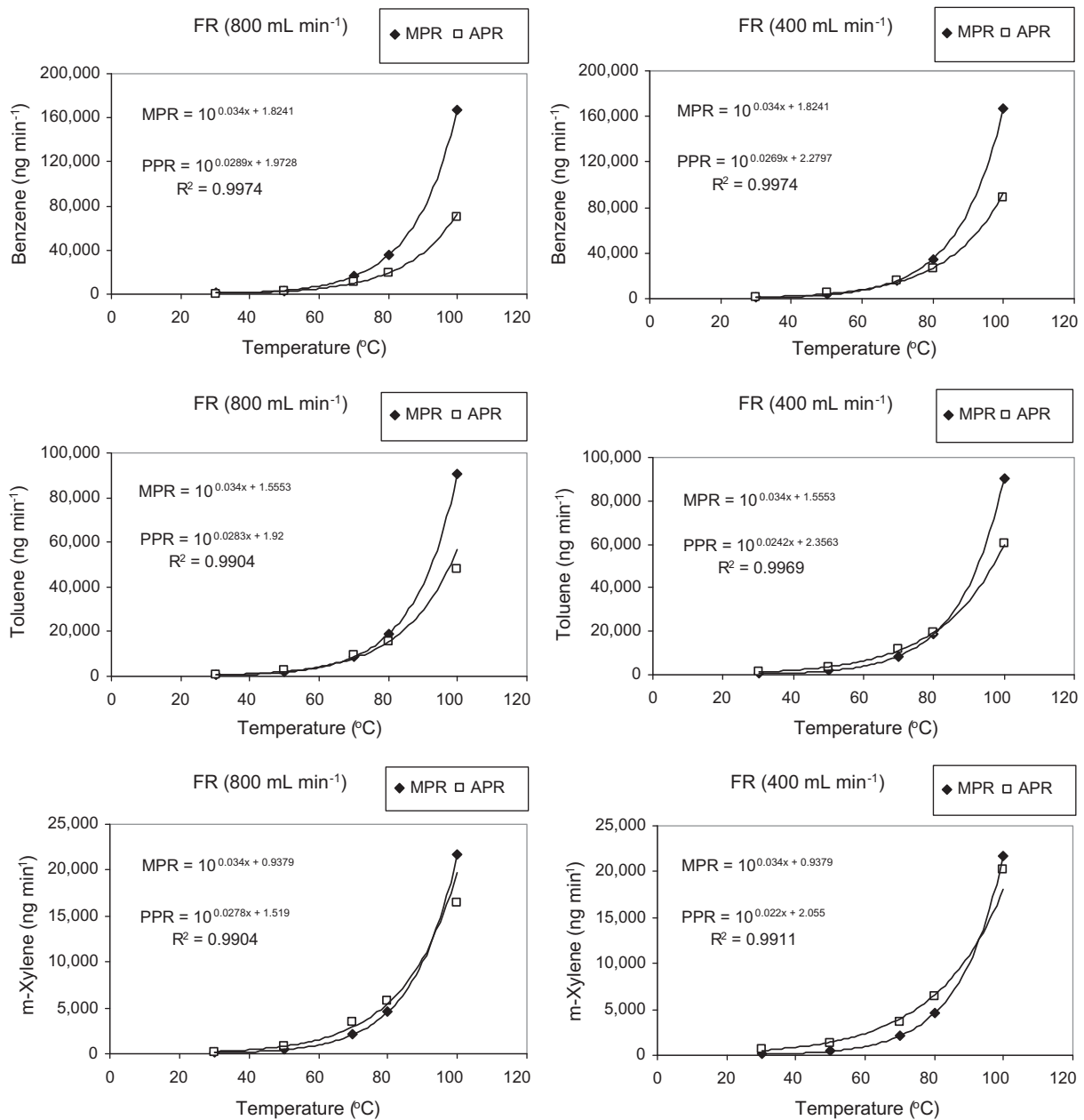


Fig. 4. Dynamic relationship between the measured permeation rate (PR: ng min^{-1}) and temperatures ($^{\circ}\text{C}$) of dilution gas by using dynacalibrator system. MPR, manufacturer-given PR; APR, actually measured PR; and PPR, predicted PR derived from our APR.

Table 4

Alternative equations derived to predict the values of concentration (PC) and permeation rate (PPR) for BTX PT devices.^a

Compound	FR 800 mL min^{-1}	R^2	FR 400 mL min^{-1}	R^2
(a) Equations to derive PC at a given temperature (T)				
B	$\log \text{PC} = 0.0289T - 0.9303$	0.9974	$\log \text{PC} = 0.0269T - 0.3224$	0.9974
T	$\log \text{PC} = 0.0283T - 0.9831$	0.9904	$\log \text{PC} = 0.0242T - 0.2458$	0.9969
X	$\log \text{PC} = 0.0278T - 1.3841$	0.9904	$\log \text{PC} = 0.0220T - 0.5471$	0.9911
(b) Equations to derive PPR at a given temperature (T)				
B	$\log \text{PPR} = 0.0289T + 1.9728$	0.9974	$\log \text{PPR} = 0.0269T + 2.2797$	0.9974
T	$\log \text{PPR} = 0.0283T + 1.9200$	0.9904	$\log \text{PPR} = 0.0242T + 2.3563$	0.9969
X	$\log \text{PPR} = 0.0278T + 1.519$	0.9904	$\log \text{PPR} = 0.0220T + 2.055$	0.9911

B = benzene, T = toluene, X = m-xylene, PC = predicted concentration, and PPR = predicted permeation rate.

^a These equations are derived empirically under the experimental setups employed in this study.

such, the APR ratios of benzene were 111 at 800 mL min^{-1} and 88 at 400 mL min^{-1} . However, its APR values at 30°C were 624 ng min^{-1} at 800 mL min^{-1} and 1105 ng min^{-1} at 400 mL min^{-1} . The existence of this compelling relationship between permeation rate and

its ratio thus indicates that the rate of PR change proceeds less dynamically at low flow rate than at high flow rate. This may be reflected by the combined effect of phenomena such as a more uniform mixing between permeant (PT) and diluent gases (N_2) at low

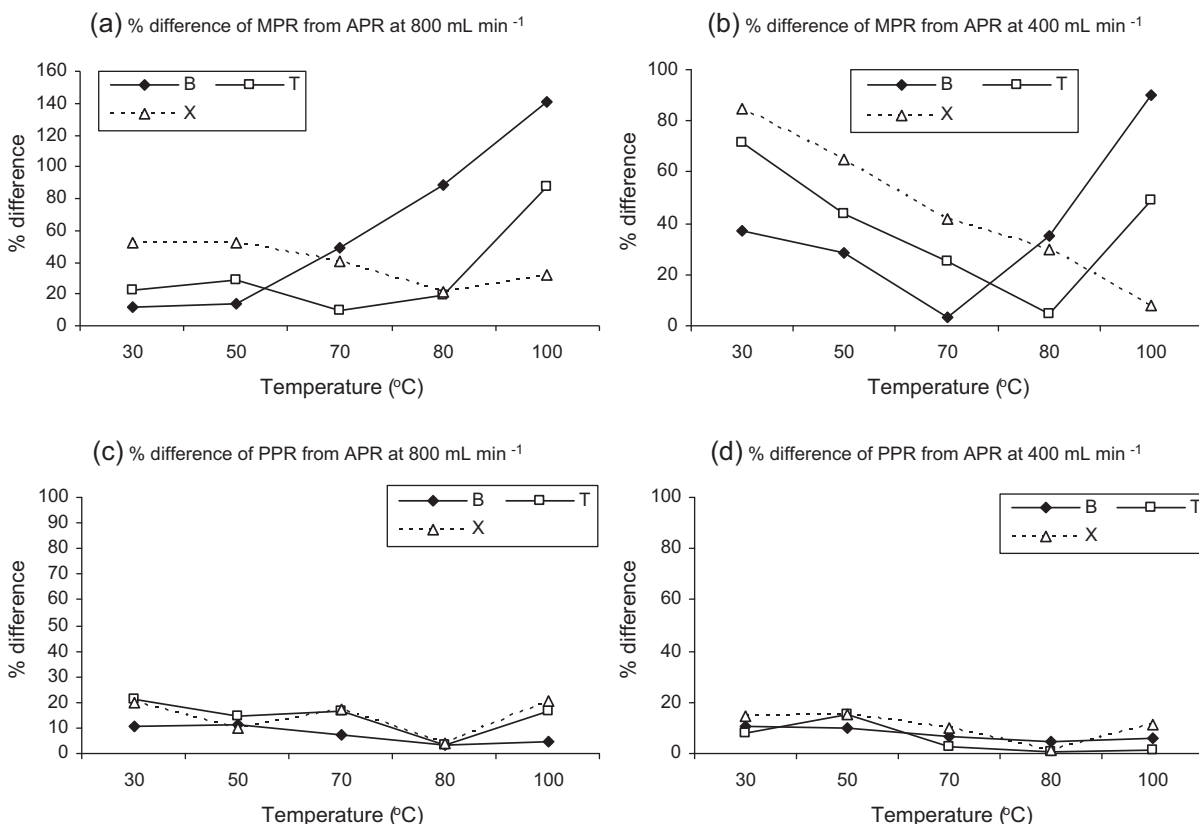


Fig. 5. A plot of the bias in terms of percent difference (%) between given (MPR) and predicted (PPR) permeation rates as a function of temperature ($^{\circ}\text{C}$). MPR, given permeation rate calculated based on the manufacturer's equation; PPR, predicted permeation rate derived from our experiment; and APR, measured permeation rate.

flow rate or the associated long contact time between them. As seen from this observation, the importance of FR control for PT application is in good agreement with the earlier investigations [12,20].

3.3. Establishment of equations for the prediction of PR (or PC)

The preceding section demonstrated the reliability of the PT device, when gas standards are generated at their respective recommended (or reference) temperature. In practice, to generate a multi-component standard gas mixture, two or more PT devices are placed simultaneously inside the chamber under a single operating temperature. Hence, the manufacturer's equation (Eq. (1)) is needed to calculate the new PR value at the given temperature. Our results show that this phenomenon will result in large deviations between APR from MPR values (and consequently the AC from MC). Hence, we developed alternative equations for each target compound to better predict the PR of PT devices.

As shown in Fig. 4, the best fit of APR values for each compound is drawn as a function of temperature to yield new empirical equations. These equations can then be used to predict permeation rate values (PPR) at specific temperatures (Fig. 4). Similarly, a plot of the logarithm of AC against temperature was used to derive predictive equations for PC (Fig. 3). High coefficient of determination from linear regression ($R^2 > 0.99$) was derived consistently for all compounds at both 800 and 400 mL min^{-1} FR in the form of:

$$\log \text{PPR} = ax + b \quad (3)$$

where PPR = predicted permeation rate (ng min^{-1}), x = temperature ($^{\circ}\text{C}$), and a and b = curve fitting parameters. The linear equation models to derive PC and PPR for each compound at both FR are

Table A.1
Calibration of BTX on the TD GC-FID system.

Order	B	T	X
(a) Information on injected analyte mass injected to the sorbent tubes (ng) using gas-tight syringe			
1	1.92	2.26	2.60
2	3.83	4.52	5.21
3	9.58	11.3	13.0
4	38.3	45.2	52.1
5	95.8	113	130
6	192	226	260
7	479	565	651
8	958	1130	1302
9	1437	1696	1954
(b) Detection limit (DL)			
ng	1.16	2.7	0.82
ppb	0.36	0.72	0.22
(c) Cylinder-based calibration results			
First (for 800 mL min^{-1})			
Slope	18,966	18,099	17,043
R^2	0.9999	0.9999	0.9882
RSE (%)	1.13	0.03	0.95
Second (for 400 mL min^{-1})			
Slope	16,611	15,468	13,465
R^2	0.9996	0.9997	0.9999
RSE (%)	0.14	0.46	1.21

presented in Table 4. These predictive equations greatly reduced the bias between expected PR values and the APR (Fig. 5). With the use of MPR, the maximum differences (%) at 800 and 400 mL min^{-1} were 141 and 90 (B), 87 and 71 (T), and 52 and 85 (m-X), respectively (Table 3). However, using our new predictive equations, the bias (%) was reduced to 4.87 and 5.66 (B), 16.7 and 8.24 (T), and 19.7 and 14.3 (m-X), respectively. Although the derived equations were

instrumental to reduce biases between APR and PPR at most temperature points, opposite trends were also seen from a few points (e.g., benzene at 400 mL min⁻¹ and 70 °C, toluene at 800 mL min⁻¹ and 70 °C, and m-xylene at 400 mL min⁻¹ and 100 °C).

If one employs this approach, the magnitude of bias in the actual application of PT device may significantly be reduced. The use of such correction equations (or factors) for permeation tubes can help reduce biases and improve the accuracy of experiments, as demonstrated in several previous studies [21,22]. Moreover, when PT devices are used over an extended period, the re-establishment of PR is recommended for a more accurate estimation of permeant concentration.

4. Conclusions

In this study, temperature was found to exert a direct effect on permeation rates of the target gases consisting of BTX generated from PT devices and consequently their concentrations. As the performances of PT devices were tested across varying temperature range, manufacturer's given equations exhibited the least bias at the manufacturer's optimum operating temperatures. As such, the standard gas generator system (i.e., dynacalibrator) exhibited high stability and reasonable RSE values when operated at the manufacturer's optimum temperatures. However, we observed that the use of MPR can result in bias if used without proper correction for the effect of temperature and flow rate. The alternative equations derived experimentally by considering measured concentration values (or the use of predicted PR (PPR)) were proven to considerably reduce biases in PT application. This approach was ideal to secure reliability of PT application in multi-component gas standards generation, which are maintained at a single point temperature that may deviate from the manufacturer's reference temperature set for the individual PT device. Finally, it is recommended that end users conduct accurate evaluations on their PT devices rather than using manufacturer supplied predictive equations, especially if operating conditions are beyond those recommended by the manufacturer.

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Appendix A. Appendices

See Table A.1.

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