original article

Evaluation of photoionization detector performance in photocatalytic studies for removing volatile organic compounds

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ABSTRACT

Aims: The aim of this study was to evaluate the performance of photoionization detector (PID) system as a substitution for gas chromatography in the measurement of a 3 xylene isomer mixtures as a representative of the volatile organic compounds in photocatalytic studies.

Materials and Methods: This study has been carried out by using test setup for generating known concentrations from equal ratio of 3 xylene isomers. The concentration values to be evaluated were classified into 4 concentration ranges from 0.1 of threshold limit values (TLV) to 2 of TLV to evaluate the PID system appliance compared with that in the reference method. The test was done 4 times for each evaluation concentration in 3 relative humidity levels (0%, 20%, and 80%).

Results: The correlation between the PID results and the National Institue of Occupational Safety and Health (NIOSH) reference method results in an atmosphere with relative humidity of 0%, 20%, and 80% were good and, respectively, were 0.993, 0.992, and 0.991 and total correlation was 0.989. The paired *t* test indicates a significant difference between actual concentrations in reference method and the extracted concentration from PID.

Conclusions: Although the results presented by PID in the present study are different from those extracted from the reference method (from 10 to 260 ppm), the equipment response is linear. So, the results are acceptable in photocatalytic studies in case the contaminant concentration is measured by the same equipment either before or after the reactor for calculation of the removal efficiency. PID calibration with the test material(s) is recommended.

Key words: Photocatalyst, photocatalytic, photoionization detector, PID, validity

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INTRODUCTION

Nano-Photocatalyst are a group of nanoscale materials that are of recent interest to many researchers in different areas, such as chemistry, chemical engineering, physics, and industrial hygiene.^[1-4]

Receiving the activation energy in a specific range of

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Rismanchian M, Golbabaei F, Mortazavi Y, Pourtaghi G, Foroushani AR. Evaluation of photoionization detector performance in photocatalytic studies for removing volatile organic compounds. Int J Env Health Eng 2012;1:42. wavelength, these materials can find the oxidation power of chemical compounds existing in the gas phase^[5.9] and liquid phase.^[10-14]

Regarding the importance of air pollution control, a major part of photocatalytic research has been allocated to building, optimizing these materials, and efficiency assessment for the control of airborne gaseous contaminants.^[15] Two types of reactors have been used in these researches, static^[16-19] and dynamic.^[20] Static reactor is composed of a closed chamber containing a specific concentration of the pollutant in which the photocatalyst is placed inside.^[21]

Gas chromatography (GC) is mostly used as an instrument measuring the pollutant concentration in this method.

In the dynamic reactor, making a known concentration of contaminant in the gas phase fluid, which is usually zero air, setting the temperature and humidity and passing the contaminant through the chamber, containing the photocatalysts, the researcher reports the removal efficiency (RE) using measurement of the pollutant concentration at both input and output of the reactor.^[20]

One of the important points in these studies is the investigation of the concentration changes during the time of passing the contaminant through the system in the presence or absence of activating spectra.^[22-24] The measurement device for assessing most of the VOCs concentration is the GC equipped with the flame ionization detector (GC-FID) or mass detector (GC-MS).^[5,19]

The GC equipments have some advantages, such as appropriate validity and accuracy, specific performance, and distinguishing the volatile organic compounds. Moreover, it is possible for GC-MS to investigate byproducts produced by photocatalytic reactions in the fluid flow.

However, there are some limitations in working with these equipments, including accessibility of them, need for highly trained operators, and the high cost of sample analysis.^[25]

The most important restriction occurs when the time length dedicated to each analysis, using this device, is more than the period of time needed to assess the photocatalysts' performance in the dynamic reactor. In other words, the researchers will feasibly lose the probability of using these systems if the retention time dedicated to the substance to be measured in GC is more than the determined intervals for concentration measurement of those substances to be tested.

The second limitation appears at the time of measuring the minimum or maximum of photocatalyst performance. In other words, if the concentration changes occur in this interval, some important data about the photocatalyst performance will be lost. These restrictions result importantly in the replacement of direct reading methods, including the use of photoionization detector (PID).

The PID acts based on the optical ionization of the airborne volatile organic compounds. Whenever an atom or molecule absorbs a photon with enough energy, loses an electron, and becomes a positive ion, ions generated in the equipment ionization chamber will be absorbed to the collection detector and the electric current proportional to the concentration of the atom or molecule will be produced. This electric current is illustrated via a monitoring system that is based on the graded concentration. Therefore, only those compounds with ionization potential less than or equal to the ionization potential of PID lamp (a UV lamp) are measurable with this device.

Recently, xylene, one the VOCs, is being commonly used in photocatalytic studies. There are 3 xylene isomers, including ortho-xylene, meta-xylene, and para-xylene selected as a model of volatile organic compounds with the ionization energy of 8.56, 8.56, and 8.445 eV, respectively, also there are the commonly used PID lamps with the ionization potential of 10.2 eV (deuterium lamp), 1.06 eV (krypton lamp), and 11.8 eV (argon lamp). Besides, each PID lamp has its own special applications.^[26-29]

Several studies in the past have focused on PID performance and applications. In the study conducted by Coffey *et al.*, 4 types of direct reading systems were compared with each other under conditions of controlled temperature, humidity, and concentration. This study in which hexan was chosen as the substance to be tested was carried out in 2 concentration ranges, 3 different temperatures, and 3 humidity levels.

Coffey *et al.* has introduced this tool as a screening device in industrial hygiene. Of all the results shown by these equipment, only 42% of the values were conformed to the reference method (in the range of $\pm 25\%$).^[30]

In the study conducted by Poirot *et al.*, the results by PID compared with those by the standard method were investigated and the findings confirmed the linearity of these 2 methods' relationship.^[26]

The PID performance was evaluated in the 2 studies carried out by Barsky *et al.*^[29] and Lee *et al.*^[28] According to their opinion, the moisture is effective on the system performance, besides, the response will be linear in case of the stability of the relative humidity. Lee *et al.* assigned that the PID values are lower than true values under each humidity condition.^[28]

It can be totally perceived that PID linear responses have been confirmed in several studies, although in some studies the results achieved by the environmental assessments have been higher than the approximation of the true value in some cases and lower than that in some others. This aim of this study was to evaluate the performance of PID system as an easily used, inexpensive equipment, which is potentially able to be as a direct reading system instead of GC equipment, which is a reference method in the measurement of a 3 xylene isomer mixture with the concentration range of 0-250 ppm and 3 humidity limits.

MATERIALS AND METHODS

Test setup

This study has been carried out by a test set up for generating known concentration. The schematic design of this setup has been illustrated in Figure 1. To perform the test, the setup was adjusted by PID system for making the concentration of xylene in the ranges of 10–20, 50–60, 105–135, and 200–260 ppm), which were considered the groups 1–4, respectively.

The equal ratio of three xylene isomers (ortho, meta, and para xylene), GC grade made by Merck Company (Germany), was used in order to make xylene and also the initial concentration was provided by making the mixture containing a certain amount of xylene with 3 isomers (ortho, meta, and para xylene) and nitrogen (N₂) with the analysis purity. The zero air and N₂ made by technical Gas Service Company with 99.999% purity grade analysis equipment were applied in this study. The concentration values to be evaluated were classified into 4 concentration ranges^[28]: 0.1 of TLV, 0.5 of TLV, 1 of TLV, and 2 of TLV.^[31] The test was done for each evaluation concentration in 3 relative humidity levels, which were 0%, 20%, and 80%. Besides, each test was repeated 4 times.^[30]

As it can be seen in Figure 1, the mixture of air-xylene with known concentration, was contemporarily exiting through 2 roots, was used for the measurement based on NIOSH 1501 as the reference method as well as the PID system.

Concentration measurement by the reference method

Recommended method NIOSH 1501 was used to measure the concentration value via the reference method.^[32]



Figure 1: Schematic diagram of making known concentration setup in gas phase

Sampling was done in 10–30 min using the activated carbon sorbent tube containing 2 sections (100 mg in the front and 50 mg in the back) of activated coconut-shell charcoal (SKC UK, NO. 226-01) as well as the low flow sampling pump (Model number 222) and air sampling pump (SKC, UK) at a flow rate of 200 mL/min.

The air sampling pump was calibrated using the electronic calibrator international Bios defender 510 UK before the beginning of each sampling section. After the sampling, the samples were prepared based on the standard method and the front and backup sections of the sorbent were analyzed separately.^[32] All samples were analyzed by using FID-equipped GC system Agilent 7890 A series with the Agilent CTC PAL autosampler injection system 6500, USA. Column Type and GC setup were Fused silica column HP-5 ms (%5 phenyl–%95 dimethylpolysiloxane; 30 m × 0.25 mm I.D, 0.25 μ m film thickness) and injector temperature:180°C, detector temperature: 250°C, oven program temperature: 60°C (2 min) to 150°C (3 min) rate 15°C/min, split ratio: 1:10, respectively.

The samples were analyzed regarding the amount of 3 xylene isomers concentration, totally and the xylene concentration in the samples was determined by using the calibration curve [Figure 2]. The breakthrough of all samples was controlled.^[32]

Concentration measurement by the photoionization detector

The measurements were contemporarily done by using Ion Science PhoCheck + PID, equipped with a 10.6 eV lamp and an internal sample draw pump with the flow of 220 mL/ min. The equipment was calibrated with isobutylene with a concentration of 100 ppm in the air and at a temperature of 20°C based on the manufacturer's instruction.

Contemporary with each sampling done according to the reference method, PID was attached to the second output of the specific concentration-making system. Furthermore,





during the sampling based on the reference method, six readings were contemporarily done with the same interval for each test and then the results were recorded.

Before the evaluation was carried out by PID, the equipment had been adjusted for reading the xylene mixture according to the manufacturer's instruction to implement the necessary correction with software for the presented values of xylene.

The temperature was fixed in 25°C during the experiment.

RESULTS

As it was mentioned earlier, after making the specific concentration in the designed setup, the passing air through the output was adjusted into 4 concentration ranges (10–20, 50–65, 105–135, and 200–260 ppm) and 3 relative humidity levels (0%, 20%, and 80%). The experiment was repeated 4 times for each case.

In Table 1, the mean and standard deviation of the presented values through the measurement of made concentrations by using both PID and the reference method are illustrated as well as the mean and standard deviation of the equipment response factor (RF), which is the ratio of the true value of the concentration in each test with the measured value by PID in the same test in terms of the relative humidity level and the concentration range.

The overall mean of the equipment response factor for all concentration ranges and humidity level was 1.29 with the standard deviation of 0.1, which means that the concentration of 100 ppm presented by PID is proportional the true concentration of 129 ppm.

The coefficient of variation (CV) mean and standard deviation in the PID results in the concentration ranges in 10–20, 50–60, 105–135, and 200–260 ppm were 4.06 (\pm 2.34), 2.29 (\pm 0.91), 2.2 (\pm 0.91), and 1.88 (\pm 0.71), respectively, besides the coefficient of variation mean was totally 2.6 with the standard deviation of 1.6.

In Figure 3a, the correlation between the values extracted from PID device and the NIOSH reference method and in Figure 3b total correlation between PID and NIOSH reference has been represented.

The correlation coefficients in all 3 humidity levels indicate a very good correlation between the results extracted from both the methods as well as the linear response of PID device.

With regard to the achieved correlation of 3 humidity levels 0%, 20%, and 80%. The following linear equations are demonstrated respectively.

A)	$Y_{\%0} = 1.124 X_{\%0} + 10.1$	$(r_1^2 = 0.992)$	(1)
B)	$Y_{\%20} = 1.254 X_{\%20} + 1.975$	$(r_2^2 = 0.991)$	(2)
C)	$Y_{\%80} = 1.247 X_{\%80} + 2.772$	$(r_3^2 = 0.993)$	(3)

The correlation linear equation between the true concentration and the concentrations by PID in different humidity levels is:

$$Y_{total} = 1.21 X_{total} + 4.784 (r_{total}^2 = 0.989)$$
 (4)

In the above equations, Y values and X values illustrate the true concentration (ppm) and the concentrations by PID (ppm), respectively.

In the Figure 4a, the conformed percent between the PID result in different humidity in Figure 4b the conformed percent between the PID result in different concentrations has been represented. The conformed criterion was \pm %25 difference between PID result and actual result.^[30]

DISCUSSION

Two types of reactors are being used in those studies related to evaluation of photocatalytic performance.

The first type is reactor with a fixed volume of several milliliters up to several liters. Regarding the volumetric flow rate of PID pump (approximately 220 mL/min), there is no possibility to apply PID in these studies. Besides, further investigation is needed in the case of other types of PID.

ranges (ppm) and humidity levels (%)						
%RH	Concentration range	Reference method Mean(SD)	PID Mean (SD)	PID Response factor Mean (SD)		
0	10-20	25.85 (4.34)	18.78 (2.66)	1.38 (0.13)		
	50-65	67.92 (6.9)	51.75 (1.61)	1.31 (0.1)		
	105-135	133.01 (8.83)	100.630 (0.6)	1.32 (0.09)		
	200-260	248.8 (6.1)	215.83 (6.08)	1.15 (0.09)		
20	10-20	12.07 (0.67)	9.57 (0.4)	1.26 (0.08)		
	50-65	63.21 (1.69)	51.97 (2.76)	1.21 (0.05)		
	105-135	141.92 (1.77)	104.29 (1.6)	1.36 (0.03)		
	200-260	273.02 (14.86)	218.54 (3.32)	1.25 (0.07)		
80	10-20	17.60 (2.19)	12.38 (0.72)	1.42 (0.17)		
	50-65	63.28 (1.85)	50.74 (0.77)	1.24 (0.02)		
	105-135	141.04 (5.33)	106.53 (6.32)	1.33 (0.04)		
	200-260	269.69 (19.18)	213.45 (5.92)	1.26 (0.08)		

Table 1: Xylene measurement results by PID system and the NIOSH reference method in different concentration

PID, photoionization detector; NIOSH, National Institue of Occupational Safety and Health.

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Figure 3: (a) The correlation between the photoionization detector (PID) results and the NIOSH reference method results in relative humidity 0% (*i*) $r^2 = 0.992$), 20% (*ii*) $r^2 = 0.991$), and 80% (*iii*) $r^2 = 993$); (b) Total correlation between PID results and NIOSH reference method results ($r^2 = 0.989$)



Figure 4: (a) The conformed percent between the PID results in different humidity levels (conform criteria = \pm %25), (b): The conformed percent between the PID results in different concentrations (conform criteria = \pm %25)

The second type of reactor is dynamics reactor in which the flow rate of air passing differentiates from few milliliters per minute (mL/min) in microreactors to 100 mL/min in common laboratory reactors. It is potentially possible to use the PID system in those researches in which the volumetric flow rate of the air passing through is higher than the flow rate of the PID internal pump.

The question is that those cases where PID can be used whether this application is correct or not.

Paired *t* test indicates a significant difference between actual concentrations in reference method and the concentration extracted from PID (P < 0.001: UCI = -30.1, LCI = -19.06, DF = 47). In other words, the results extracted from these 2 methods are not identical.

This finding may be due to this matter of fact that the calibration of the equipment is done according to manufacturer's instruction, which is based on the concentration of iso- buthylene which is 100 ppm. This difference among the results is conformed with the studies conducted by Poirot *et al.*,^[26] Lee *et al.*^[28] and Coffey *et al.* moreover, although the correction factor^[30] related to the calculating of 3 xylene isomers has been interfered, there is still the difference between the results. This differentiation among the results is similar to those results extracted from the studies conducted by Poirot *et al.*^[26], Lee *et al.*,^[28] and Coffey *et al.*^[30]

The equipment response in terms of different concentrations and humidity levels was also investigated in this study. The correlation coefficients obtained in the range investigated are 0.992, 0.991, and 0.993 in the presence of humidity levels 0%, 20%, and 80%, respectively, which in all 3 cases represents the completely linear changes in the results achieved by PID system in comparison with the actual concentration values.

The total correlation coefficient between the results of all PID measurements and actual concentration values is 0.98.

This correlation coefficient indicates that except the

humidity level, there is an acceptable linear relationship between PID system results and actual concentration values.

A little decrease in correlation coefficient illustrates a slight impaction of moisture on the system performance.

There are also similar correlation coefficients reported in the studies conducted by Lee *et al.*,^[28] Barsky *et al.*,^[29] Poirot *et al.*,^[26] and Coffey *et al.*,^[30] Of course, in the study reported by Barsky *et al.*, the fluctuated humidity level has been effected on PID lamps with the ionization energy of 11.8 and 10.2 eV.^[29]

The calculation of ionization equipment response factor (the ratio between the actual concentration and the concentration shown via PID) results in 1.29, which indicates a 29% difference during equipment calibration by iso-butylene.

Moreover, the variance analysis of the result shows that in each concentration group. There is no significant difference among the response factors obtained from PID in different humidity levels.

Coffey *et al.*^[30] inferred that these results were basically extracted due to the kind of material composition, also in the Barsky *et al.*'s research,^[29] which was performed on some compounds except xylene, the moisture was founded as an effective parameter on the response of PID equipment.

The evaluation of changes, coefficient of variation (CV) related to those results obtained from PID equipment represent the decrease in CV with increasing of the reading concentration values. In other words, at higher concentration, more repeatable measurements are possible to be done by this equipment and the lower standard deviation will be achieved in this situation. Conversely, at lower concentrations the results show the lower repeatability as well as greater differences. Therefore, at lower concentration values (<10 ppm), PID should be used with higher considerations.

Regarding the mentioned conditions, how does the contaminants removal take place in the field of photocatalysis.

The RE in the researches related to photocatalysis performance is essentially calculated by the following equation:

$$\%RE = \frac{C_{\text{inlet}} - C_{\text{outer}}}{C_{\text{inet}}} \times 100$$
(5)

Where

 C_{inlet} = concentration at the inlet of the reactor. C_{outlet} = concentration at the outlet of the reactor.

Moreover, in each specific concentration, multiplying one certain multiplier in all parameters above makes no changes in the equation results.

Although in those studies in which the adsorption capacity

has been considered, the calculated efficiency using Eq. (5) will decrease in terms of increasing the contaminant concentration. In this situations case-calibration of PID equipment with the pollutant seems really essential.

This inference is similar to one substance in the study conducted by Coffey *et al.*^[30] as well as a mixture of materials in the study done by Poirot *et al.*^[26]

In this article, the literature review was carried out on the previous studies in which the advantages and disadvantages of photoionization system in various fields of industrial hygiene were discussed. Besides, it has been illustrated that while the results presented by PID (in range 10–260 ppm) are different from those extracted from the reference method, the equipment response is linear except for humidity level.

Thus, the results are acceptable in photocatalytic studies in case the contaminant concentration is measured by the same equipment either before and after the reactor and only thing which is due to be considered is the RE. Totally, PID calibration with the test material(s) is recommended.

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