Pergamon

S0045-6535(96)00107-5

Chemosphere, Vol. 32, No. 10, pp. 2057–2065, 1996

0045-6535/96 $15.00+0.00

Collection and Determination of 4,4'-Bipyridine Vapor Using XAD-2 Resin

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(Received in USA 15 August 1995; accepted 19 February 1996)

ABSTRACT

A vapor generation system, using a permeation tube to produce 4,4'-bipyridine vapor, was designed to evaluate the collection efficiency (CE) of XAD-2 resin. At less than 10% relative humidity, collection efficiency was found to be 94.7%±2.1%. At greater than 90% relative humidity, CE was slightly reduced to a level of 80.5%±4.8%. The results of a breakthrough study indicate that in 5 successive collections from the XAD-2 collection tube, less than 2.6% of the total 4,4'-bipyridine volume was released. A comparison of XAD-2 resin collection results with estimations based on gas saturation (GS) suggests that XAD-2 resin is an effective sorbent for collecting 4,4'-bipyridine. The authors concluded that XAD-2 resin is well-suited for use in systems to measure personal exposure to 4,4'-bipyridine vapor. Copyright © 1996 Elsevier Science Ltd

Key words: 4,4'-bipyridine, XAD-2 resin, collection efficiency

INTRODUCTION

One of the primary herbicides currently used in Taiwan is paraquat dichloride.[1] It is considered an effective herbicide, but the major intermediate product, 4,4′-bipyridine, is postulated to be harmful to humans.[2] A 1982 study by Bowra et al. studied workers in a paraquat factory. He reported that coal tar or other intermediate products can cause premalignant and malignant skin lesions in exposed workers.[3] Li, in 1984, studied several cases of malignanat skin lesions in paraquat workers.[4] Wang et al., in 1987, investigated the role of bypridine in the production of malignant and premalignant skin lesions in paraquat factory workers. Furthermore, 4,4′-bipyridine may be harmful to humans if inhaled, ingested or absorbed through the skin.[5]

The authors previously developed and evaluated an air sampling method, using XAD-2 collection tubes and a U-tube dynamic sampling system.[6] This was a relatively simple system for the collection of organic compounds, with many methodological limitations.[7] The limitations include difficulty controlling and determining the exact amount of vapor released which makes it problematic to evaluate breakthrough times for the collection medium. Thus it was the authors′ desire to work with a more complex system to allow for a more complete study.

As noted in a previous study,[8] 4,4′-bipyridine can exist in both aerosol and vapor phases. On average, the mass ratio of vapor to aerosol was found to be 0.025. The authors decided that for this study the most important issue was measurement of the vapor-phase portion of 4,4′-bipyridine, because currently, there is no standard recognized method for the collection of 4,4′-bipyridine vapor. In the current study, a vapor generation system, using a permeation tube for gas generation, was employed. This system is a more complex and flexible system, allowing for additional tests to be performed. The objective of this study was to evaluate collection efficiency at varying concentrations of 4,4'-bipyridine vapor and two levels of humidity within the system. The study compared field sampling concentrations with values estimated through the use of the gas saturation method.

METHODS

Instrumentation

Using a U6k injection valve and ultraviolet detection at 254 nm wavelength, a high-performance liquid chromatograph(model 441, Water Assoc.,Inc) was employed under the following conditions: mobile phase 50/50 MeOH/H_2O, flow rate 0.6 mL/min,and chart speed 1 cm/min. A stainless steel column (ID 4.6 mm*150 mm) was packed with inersil ODS2 (octadecyl-bonded silica gel, Gasukuro Kagyo Inc, Tokyo, Japan). The absolute retention time for the peak of 4,4-bipyridine was 4.9 min. Instruments were tested and found to produce results that were both highly reliable and highly reproducible.[6] These instruments were evaluated in a previous study by the same authors.

Collection efficiency and breakthrough study

All tests were performed at room temperature (25-27°C). The relative humidity was set at either <10% or >90%. The generated level of 4,4'-bipyridine vapor was estimated based on the permeation tube values. The vapor generation system is shown in figure 1. At each humidity level and generated vapor level, collection efficiency was measured by comparing the initial gas amount (ug/m^3) from the permeation tube (Dynacal permeation device, VICI Metronics, Santa Clara, California) with the amount (ug/m^3) collected in XAD-2 solid sorbent. XAD-2 is a non-polar resinous compound composed of copolymerized styrene and divinyl benzene. Henriks-Eckerman,[9] in 1990, reported using XAD-2 to replace charcoal for the collection of organic air pollutants. In 1982, Spitzer reported using XAD-2 to separate polyaromatic hydrocarbons.[10] A breakthrough study of the XAD-2 tube was also performed. After the 4,4'-bipyridine entered the XAD-2 tube, at permeation, there was a small amount of gas which would escape through the XAD-2 tube. This breakthrough gas was collected 5 times and its volume was measured. The 4,4'-bipyridine residue on the breakthrough gas collection tubes was also measured. Finally, the actual amount of 4,4'-bipyridine collected in the XAD-2 tube was measured. Thus the overall recovery rate was calculated by combining these measures. Finally, a comparison of 4,4'-bipyridine concentration through estimation by gas saturation (GS) and field sampling was conducted. Two temperature levels were chosen (20 and 27 °C) and two samples were taken at each temperature. These results were compared with concentration values obtained through GS estimation.

RESULTS AND DISCUSSION

Collection efficiency

The collection efficiency of XAD-2 resin was tested at two different humidity levels (see Table 1). At humidity levels less than 10% relative humidity, the mean collection efficiency was 94.7 %±2.1 %. At humidity levels above 90 % relative humidity, the collection efficiency was 80.5 %±4.8 %. These results suggest an inverse relationship between collection efficiency and relative humidity. Furthermore, it was noted that there is a direct relationship between relative humidity and the range of collection efficiencies. This can be seen in the higher S.D. (4.8 compared to 2.1) at the higher humidity level. Therefore, increasing levels of humidity cause a decrease in the efficiency and the reliability of 4,4'-bipyridine collection. It should be noted that in the authors' opinion, XAD-2 is an ideal sorbent for the collection of 4,4'-bipyridine. In both this study and previous studies[6] by these authors, it is clear that regardless of the collection system(U-tube dynamic sampling or permeation tube vapor generation system) that is used, XAD-2 makes an ideal collection medium.

Table 1. Efficiency of an XAD-2 tube for collection of 4,4'-bipyridine at two humidity levels(n=3)

Humidity (RH %)	Generated 4,4'-bipyridine ug/m^3	Collection Efficiency (%)
< 10	6.3	93.4
	8.6	93.3
	23.0	93.8
	30.0	98.4
		mean 94.7±2.1
>90	14.0	80.9
	20.0	76.6
	28.0	81.1
	33.0	83.8
		mean 80.5±4.8

Breakthrough Study

The study was conducted using additional tubes to collect any evidence of breakthrough 4,4'-bipyridine, thus determining the collection capacity of the XAD-2 tubes. The results of the study are shown in Table 2. Five tubes were used; each one for a period of two hours, for a total trial time of 10 hours. The gas flow was set at a volume of 200 cc/min. The total volume of air to pass through the system was 120 liters. For the three trials conducted, the overall recovery was 95.7%. The recovery percentage is the amount of 4,4'-bipyridine vapor actually collected by the XAD-2 resin, as a percentage of the initial amount of vapor released. The collection amount is the absolute amount of 4,4'-bipyridine collected in the XAD-2 resin. It was observed that as the time progressed, the amount of breakthrough 4,4'-bipyridine increased slightly. One possible reason for the appearance of breakthrough 4,4'-bipyridine is the flow rate. An increase or decrease in flow volume and/or rate may affect the breakthrough volume. Furthermore, the appearance of XAD-2 residue, from 1.05 % to 1.60 %, on the non-collection portion of the test-tube wall, suggests that it is important to clean the test-tube walls, during studies and/or practical usage of these systems. The authors wish to point out that further study of this topic is necessary, specifically with regards to higher levels of relative humidity and longer periods of time. Previously, it was established, in the absence of a threshold limit value, that the tentative standard for 4,4'-bipyridine is 0.1 mg/m^3 (respirable)[11]. Using this standard, it is possible, using an XAD-2 collection tube, to collect at least 500 liters of air before reaching this level.

Table 2. Breakthrough study of 4,4'-bipyridine vapor from XAD-2 tube

auxiliary tube number	I	II	III	mean
1	0.051(0.09)*	0.045(0.08)	0.030(0.06)	0.042(0.08)
2	0.094(0.16)	0.098(0.19)	0.069(0.14)	0.087(0.16)
3	0.127(0.22)	0.127(0.24)	0.100(0.19)	0.118(0.22)
4	0.137(0.24)	0.130(0.25)	0.118(0.23)	0.128(0.24)
5	0.198(0.34)	----	0.210(0.41)	0.136(0.25)
Residue**	0.611(1.05)	0.976(1.80)	0.811(1.60)	0.803(1.48)
Coll. amt.	57.2(98.3)	52.3(97.4)	50.33(97.4)	53.3(97.7)
Recovery(%)	102.2	94.2	90.5	95.7 ± 4.9

* amount of 4,4'-bipyridine (%)
** residual amounts of 4,4'-bipyridine in XAD-2 tube wall
Collection amount: the amount of 4,4'-bipyridine vapor collected by the XAD-2 resin
Recovery(%): 4,4'-bipyridine collected by the XAD-2 resin, as a percentage of the original amount of gas released.

Comparison of field study with gas saturation method

The field study was conducted in a paraquat manufacturing plant. The authors were given access to a 4,4'-bipyridine tank, which was opened to provide a vapor source for collection. Table 3 shows a comparison of the values obtained. The sampling was done at two temperature levels, 20 °C and 27 °C. The collection volume was directly related to the temperature. The reliability of the collection volume was inversely related to the temperature. Thus at higher temperatures, more gas was released and the collection efficiency was more variable. The collection volumes in the field study were compared with values obtained through the use of the gas saturation method.[12] The gas saturation method was originally used to determine the vapor pressure of 4,4'-bipyridine and it can be used to estimate the amount of gas released under a certain set of conditions. A comparison of the values yielded ratios between 98.1 % and 111.2 %, thus the authors concluded that the field sampling

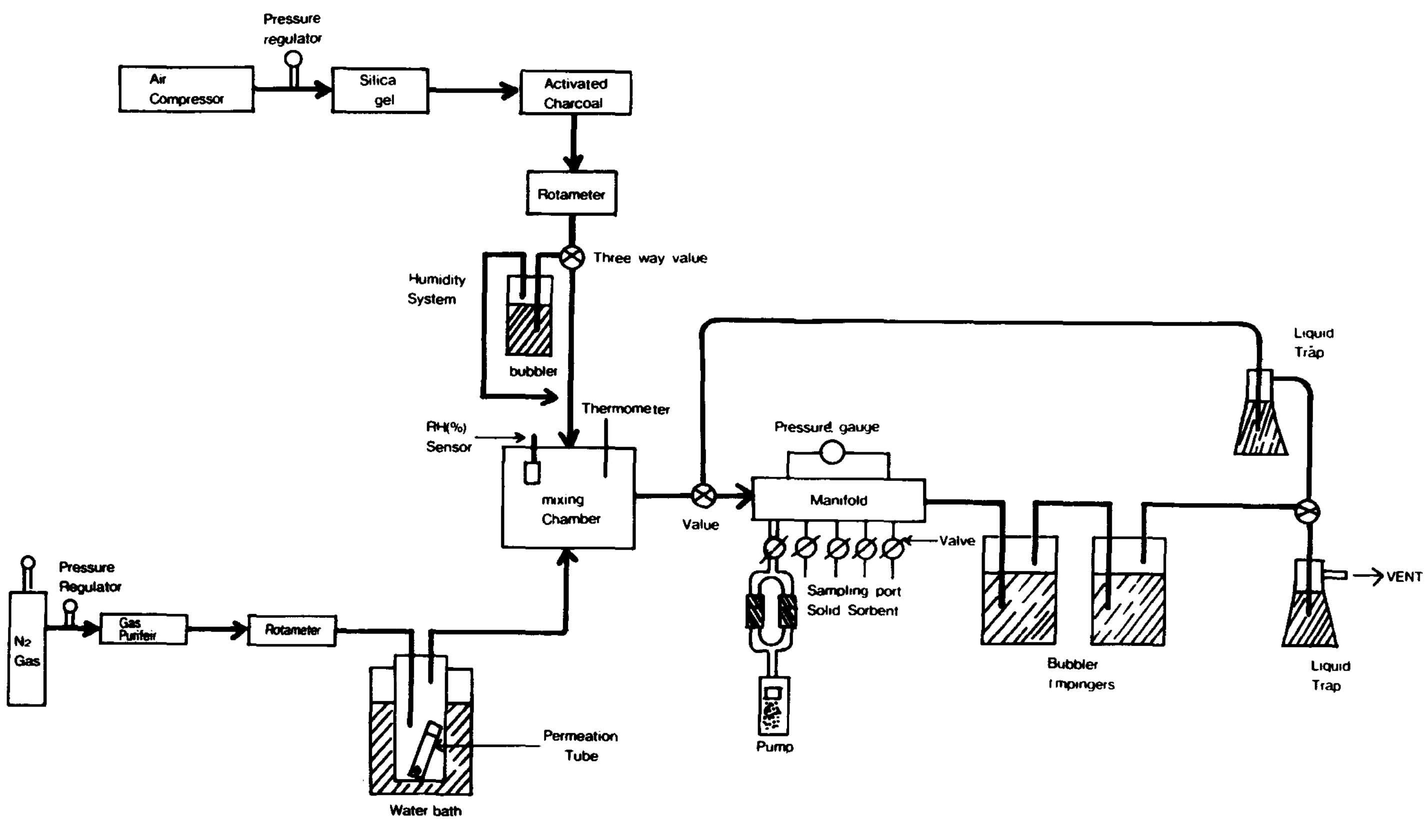

Figure 1. Schematic apparatus for 4,4'-bipyrindine vapor generation system

method was able to yield reliable collection results.

Table 3. Comparison of measurement of 4,4'-bipyridine vapor(mg/m^3) between field sampling and estimation by gas saturation (GS)

Temp.(°C)	field sampling	GS method	ratio(%)
20	0.450	0.450	100.0
	0.453	0.453	100.6
27	1.190	1.070	111.2
	1.050	1.070	98.1

CONCLUSION

A study of XAD-2 resin used in a system to measure exposure to 4,4'-bipyridine showed that collection efficiency is highest at low levels of humidity. Using a TLV (threshold limit value) of 0.1 mg/m^3, it was determined that a volume of at least 500 liters of air can be collected, without passing the TLV due to breakthrough. Finally, a comparison of field sampling with gas saturation methods, showed that field sampling can yield reliable collection results.

ACKNOWLEDGMENT
This study was supported by a special grant from National Science Council 80-0421-B002-13Z.

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