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New Method for Spectrophotometric Determination of Allyl Alcohol Using Aryl Aldehydes as Reagents

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The method is based on condensation reaction of allyl alcohol with aryl aldehydes to form red-purple coloured derivatives having maximum absorbance at 555 nm. The colour system obeys Beer's law in the range till 7.5 μg of allyl alcohol in 25 ml of final solution. The molar absorptivity and Sandell's sensitivity were found to be 15.3×10^3 l mol^{-1} cm^{-1} and 0.004 μg cm^{-2}, respectively. The standard deviation and relative standard deviation of absorbance values were found to be 0.09 and 1.8%, respectively for 7 replicate analyses. 3,4-Dimetoxybenzaldehyde and 4-methoxybenzaldehyde have been investigated as reagents. The effect of analytical parameters and diverse ions was evaluated. The method has been applied for the determination of allyl alcohol in water, plant materials and air. The method is simple, sensitive and more selective than other reported methods.

Metoda polega na kondensacji alkoholu allilowego z aldehydami aromatycznymi z wytworzeniem barwnych produktów o maksimum absorpcji przy długości fali 555 nm. Układ spełnia prawo Beera do zakresu 7,5 μg alkoholu allilowego w 25 ml końcowego roztworu. Molowy współczynnik absorpcji i współczynnik czułości Sandella wynoszą odpowiednio $15{,}3 \times 10^3$ l mol^{-1} cm^{-1} i 0,004 μg cm^{-2}. Odchylenie standardowe i względne odchylenie standardowe wartości absorbancji wynoszą odpowiednio 0,09 i 1,8% dla siedmiokrotnych oznaczeń. Jako odczynniki zastosowano 3,4-dimetoksybenzaldehyd i 4-metoksybenzaldehyd. Oszacowano wpływ parametrów oznaczania i różnych substancji towarzyszących. Metoda została zastosowana do oznaczania alkoholu allilowego w wodzie, materiale roślinnym i powietrzu. Metoda jest prosta, czuła i bardziej selektywna od innych znanych metod.

Allyl alcohol (2-propene-1-ol, vinyl carbinol) is one of the extensively employed organic chemicals for the preparation of allyl resins, plastics and pharmaceuticals [1].

It is also used as a herbicide in several parts of the world [6]. Occupational exposure to allyl alcohol is very common and cause manifested lacrimation, retrobulbar pain, photophobia and vision troubles [2]. Looking to its extreme toxicity to human beings the permissible exposure limit value has been set at 2 ppm (5 mg m^{-3}) by OSHA as well as ACGIH [3,4]. Though the toxicology of the compound is well established only few methods are avilable for its quantitative estimation. The most popular methods are based on iodometry [5] and colorimetric determination using vanilline (3-methoxy-4-hydroxybenzaldehyde) as reagent [6]. These methods suffer from several disadvantages.

Considering the need for a new method the reaction between allyl alcohol and aryl aldehydes has been investigated and a new spectrophotometric method has been developed for the determination of allyl alcohol. As reagents were investigated aryl aldehydes: 3,4-dimetoxybenzaldehyde or 4-methoxybenzaldehyde which in conc. sulphuric acid form a red-purple product with maximum absorbance at 555 nm. The method has been applied for the determination of allyl alcohol in water, air and plant materials.

EXPERIMENTAL

Apparatus and reagents

Calibrated rotameters (PIMCO) and 35 ml midget impingers were used for air sampling. Spectral and absorbance measurements were made with Carl Zeiss spectrophotometer with 10 mm optically matched silica cells.

All chemicals used were AnalaR grade unless otherwise stated.

Doubly distilled deionized water was used throughout the study.

Allyl alcohol: 1 mg ml^{-1} stock solution was prepared from freshly distilled allyl alcohol. Working solution (1 μg ml^{-1}) was prepared by appropriate dilution.

3,4-Dimetoxybenzaldehyde – DBH (Aldrich): 0.05%(m/V) solution in 72% sulphuric acid.

4-Metoxybenzaldehyde – MBH (Aldrich): 0.5%(m/V) solution in 72% sulphuric acid.

Procedure

Preparation of calibration graph: 0, 0.5, 1, .. 5 ml of working solution were pipetted into a series of 25 ml calibrated graduated tubes. Then 0.5 ml of DBH or MBH reagent was added followed by 5 ml of conc. sulphuric acid. The tubes were then placed in a boiling water bath for 2 min. Next they were taken out, cooled and their contents were diluted to the mark with 0.001 mol l^{-1} sulphuric acid. Absorbance was measured at 555 nm against a reagent blank.

Determination of allyl alcohol in air: Air containing allyl alcohol was drawn through two midget impingers, containing 5 ml of water connected to an air sampling train [7,8] at a flow rate of 1 l min^{-1} for 15 min. After sampling an aliquot of the sample was quantitatively transferred to a 25 ml graduated tube and then analysed as recommended above.

Determination of allyl alcohol in plant materials: Different concentrations of allyl alcohol solutions were sprayed over 500 g of plant materials and allowed to stay for ~1 h. Then allyl alcohol present in the spiked samples was extracted with 10 ml of water. An aliquot of this solution was transferred into a graduated tube and analysed as recommended above.

RESULTS AND DISCUSSION

The absorption spectrum of the red-purple chromogen exhibits maximum absorbance at 555 nm while reagent blank shows negligible absorbance at this wavelength. The colour system obeys Beer's law in the range up to 7.5 μg of allyl alcohol in 25 ml of final solution. The molar absorptivity of the colour system is 15.3×10^3 l mol^{-1} cm^{-1}. The Sandell's sesitivity was found to be 0.004 μg cm^{-2}.

The condensation reaction initially requires high acidity maintained by conc. sulphuric acid. The final pH of the coloured solution was between 0.5 and 2.

Effect of different temperature and time intervals on colour development were studied. It was found that the colour develops immediately at 80–100°C. In the boiling water bath 2 min were sufficient for complete reaction.

Under optimum conditions 1 ml of 0.5% of MBH or DBH was necessary for complete colour development. Any increase of the reagent concentration affects the reproducibility of the reaction due to self condensation of the reagents.

Collection and absorption efficiency of allyl alcohol vapours was studied by methods cited in literature [7,8]. Under the optimum conditions water can completely absorb the vapours of allyl alcohol. Absorption was nearly 100% in first impinger. The effects of flow rate and time of sampling were also evaluated. It was found that flow rate of 1 l min^{-1} for a 15 min sampling period are the best.

The effect of diverse substances likely to interfere with real sample analysis was investigated. Most of the organic, inorganic and metal ions do not interfere with the method. The tolerance limit for 5 μg of allyl alcohol in 25 ml (in μg ml^{-1}) are as follows: ethanol, hexanol (3500), aniline, pyridine, phenol (1500), furfural (300), formaldehyde (100), propanol, butanol (50).

Reproducibility of the method has been assessed by analyzing 5 μg of allyl alcohol for a period of 7 days. The standard deviation and relative standard deviation of absorbance values were ± 0.09 and 1.8 % respectively for 7 replicate analyses.

The proposed method has been applied for the determination of allyl alcohol in polluted water, plant material and air. As laboratory air did not contain allyl alcohol the allyl alcohol vapours were generated by reported methods [7,8]. The results obtained were also compared with reported vanilline method (Table 1).

Table 1. Results of analyses of environmental samples

Sample		Allyl alcohol added, μg	Allyl alcohol found, μg	
			proposed method	vaniline method
1		2	3	4
Polluted river water	A_1	0.00	0.00	0.00
	A_2	1.50	1.46	1.38
	A_3	4.00	3.93	3.91
	A_4	5.00	4.96	4.96
	A_5	6.00	5.95	5.80
	A_6	7.50	7.48	7.05

Table 1 (continued)

1		2	3	4
Plant material	B_1	1.50	1.33	1.23
	B_2	3.00	2.64	2.62
	B_3	4.50	4.40	4.15
	B_4	6.00	5.51	5.01
	B_5	7.50	7.45	7.30
Air	C_1		0.55	0.39
	C_2		3.60	3.60
	C_3		2.41	2.12
	C_4		5.09	4.95
	C_5		5.04	4.93

Conclusion

The proposed method is simple, rapid and sensitive. It is more reproducible than reported vanilline method. The method has been found to be suitable for industrial hygiene determinations.

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