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Detection of Acrylonitrile and Ethylene Oxide in Air and Fumigated Foodstuffs

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Acrylonitrile has wide industrial applications such as in the manufacture of acrylic fibers, plastics and as a chemical intermediate in the synthesis of antioxidants, pharmaceuticals, dyes, etc. (CHEMISTRY OF ACRYLONITRILE 1959). Ethylene oxide is used in sterilizing surgical appliances, and in organic syntheses (MERCK INDEX 1976). Both acrylonitrile and ethylene oxide are used as fumigants in combination with nonflammable adjuvants (MONRO 1969). Recently the carcinogenic risks of acrylonitrile from excessive exposures have been reported (MALTONI et al. 1977). Ethylene oxide is included in the list of suspected carcinogens (FAIRCHILD 1978). The time-weighted average concentrations for exposure to acrylonitrile and ethylene oxide have been fixed as 2 and 50 ppm, respectively (FEDERAL REGISTER 1978, FAIRCHILD 1978).

A simple paper-strip method to detect acrylonitrile and ethylene oxide in air and fumigated foodstuffs is reported here.

MATERIALS AND METHODS

Preparation of Detector Strips. A reagent containing 2% anhydrous sodium sulfite and 1:3 thymol blue-phenolphthalein mixed indicator was prepared as follows. About 2 g anhydrous sodium sulfite was dissolved in 50 mL of distilled water and 25 mg thymol blue plus 75 mg phenolphthalein were dissolved in 50 mL of distilled ethanol. The indicator mixture was added to the sulfite solution and mixed well. Filter paper strips (Whatman No. 1) of 7 x 3 cm were individually dipped in the reagent and placed near a circulating fan for drying. Then the strips were kept in a polyethylene pouch. The prepared strips were used within 3 days.

Detection in Air. A detector strip was placed in a 20-mL hypodermic syringe, the plunger was pushed to the 10-mL mark and the syringe was plugged with a rubber septum. Acrylonitrile vapor was taken from a saturated vapor reservoir (RAJENDRAN & MUTHU 1981) with a hypodermic or microsyringe for dosing the test syringes. Ethylene oxide (100%) gas was similarly drawn from a 1-kg cylinder without the siphon tube and dosed. Besides the saturated concentrations, acrylonitrile concentrations in the range of 0.17-19.5 g/m^3 and ethylene oxide 0.79-80 g/m^3 were tested at the laboratory temperature of 27.1 ± 1°C and 70 ± 6% relative humidity (RH). At the end of 30 min the colors of the strips were matched with the color plates in the Dictionary of Color (MAERZ & REA PAUL 1950)

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against a gray background. The color of the strips exposed to air were identified with the horticultural colours also (WILSON 1938). There were duplicates for each concentration range besides a control. The detector reagent was prepared twice and two experiments were conducted on each occasion. Thus, there were totally eight replicates per concentration range and for unfumigated control.

The detector strip was also tested with the saturated concentrations of fumigants acetonitrile, carbon tetrachloride, chloroform, carbon disulfide, ethylene dichloride, ethyl and methyl formates, methyl bromide, methyl iodide, dichloromethane, phosphine, propylene oxide, sulfur dioxide, trichloroethylene and (100%) carbon dioxide. In the syringe containing the detector strip the plunger was pushed as far as it could go and saturated vapor or carbon dioxide was drawn in up to the 20-mL mark. After 30 min the color was scanned as above.

Detection in Foodstuffs. Paddy, wheat, polished raw rice, semolina, split chickpeas, curry powder and dry dates each weighing 75 g were fumigated for 24 h at the effective dose of 50 g/m^3 of acrylonitrile and ethylene oxide in 125-mL gas-wash-bottles at 25-30°C and 40-90% RH. For each fumigant, there were two replicates per commodity. Untreated controls were run concurrently. The fumigated commodities were aerated for 24 h. A detector strip was kept in the side limb of each gas-wash-bottle and it was stoppered.

The gas-wash-bottles containing the foodstuffs fumigated with acrylonitrile were placed in a water-bath maintained at 80°C and that with ethylene oxide at 40°C for 30 min to accelerate the desorption of unaired residues. Gas analysis was conducted by GLC with a FID using a 15% Carbowax 1500 on 80-100 mesh Celite column. The temperatures were as follows: injector 77, oven 42 and detector 119°C. Nitrogen flow rate was 27 cc/min. The desorbed residues were estimated for the volume of the gas-wash-bottles with load (MUTHU et al. 1978). The detector strips were taken out and the color shades noted.

RESULTS

The original color of the detector strip i.e. 'polar-bear' - plate 9 B2 (MAERZ & REA PAUL 1950) or 'maize yellow' - 607/3 (WILSON 1938) did not change in air. In the presence of acrylonitrile and ethylene oxide, however, it changed to pink, rose, purple and violet depending on the concentrations of the fumigants. The exact color of the strip as read in the Dictionary of Color is given in Table 1. The minimum detectable concentration by this method was 0.34 g/m^3, for acrylonitrile and 1.58 g/m^3 for ethylene oxide. Nevertheless, very distinct color changes occurred when acrylonitrile concentrations were $\geq$1.36 g/m^3 and ethylene oxide concentrations were $\geq$6.32 g/m^3.

The detector strip failed to show a change in its original color in the presence of saturated vapors of other fumigants except

Table 1. Color of the detector strip at different concentrations of acrylonitrile and ethylene oxide in air in 30 min at 27.1 ± 1°C.

Fumigant Concentration (g/m^3)	Color of the strip as read in the Dictionary of Color* (no. observations in parentheses)	
	Acrylonitrile	
0	9B2 (8)	
0.17-0.20	9B2 (8)	
0.34-0.40	9A2 (6)	9B2
0.68-0.80	9A3 (3)	9A2 (3), 10A2, 42B1
1.36-1.60	42B1 (4)	9A3 (2), 1D7, 1A8
1.70-2.00	41D1 (4)	42B1 (2), 1A8 (2)
3.40-3.90	41F4 (5)	41E3 (2), 41H6
6.80-7.80	41H7 (6)	41H6, 41I7
13.60-15.60	41I8 (5)	41H8 (2), 41H7
17.00-19.50	41I8 (3)	41H8 (3), 41H7
345-380	41H10 (4)	41J10 (3), 41H9
	Ethylene oxide	
0	9B2 (8)	
0.79-0.80	9B2 (5)	9A2
1.58-1.60	9A2 (5)	9A3 (3), 10A2
3.16-3.20	9A3 (4)	10A2 (2), 1A8, 2B7
6.32-6.40	1D1 (3)	1D7 (2), 1E7 (2), 1A8
7.90-8.00	1C7 (5)	1E7 (2), 41C1
15.80-16.00	41E2 (6)	41F4, 1A3
31.60-32.00	41G5 (5)	41H6 (2), 41C1
63.20-64.00	41H7 (6)	41H6, 41I7
79-80	41H7 (6)	41I8
1550-1610	41F8 (5)	41E8 (2), 41I7

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* MAERZ & REA PAUL 1950

propylene oxide. Carbon dioxide also had no influence on the color of the detector strip.

The desorbed residues of acrylonitrile and ethylene oxide from the commodities as determined by GLC were also detected by the strips. The strip detected as low as 1.68 ppm of desorbed acrylonitrile and 0.73 ppm of ethylene oxide residues at 80 and 40°C, respectively.

DISCUSSION

To detect acrylonitrile or hydrogen cyanide in air (MCCONNAUGHEY (1955) used a reagent consisting of O'-toluidine, anhydrous copper sulfate and glycerol on an inert carrier like silica gel. The use of water soluble salt, like potassium iodide, stannous chloride, potassium thiocyanate, magnesium bromide or disodium hydrogen phosphate with a suitable acid-base indicator was recommended for the detection of ethylene oxide in air or in aqueous solutions (MINNESOTA MINING & MANUFACTURING CO. 1960). SUMIMOTO & KOHAMA (1978) used an indicator compound comprising 4-(4'-nitrobenzyl)pyridine, nitro-cellulose, a basic substance and a blue coloring agent which turns from blue to green after exposure to 1:8 ethylene oxide-carbon dioxide mixture in 30 min. Dräger and Kitagawa detector tubes are available for the detection and estimation of approximate concentrations of various fumigants including acrylonitrile and ethylene oxide in air (DUMAS & MONRO 1966). But underdeveloped and developing countries may find it difficult to import such detector tubes for routine fumigation jobs.

The present method is based on the reaction reported by TERENTÉV & OBTEMPERANSKAYA (1956) for the determination of acrylonitrile in solutions: $CH_2{:}CHCN + Na_2SO_3 + H_2O \rightarrow CH_2(SO_3Na)\ CH_2CN + NaOH$. Similarly, sodium hydroxide is formed in the reaction between ethylene oxide, sodium sulfite and the moisture in the detector strip. Evidently, the moisture in the detector strip is an important factor for its sensitivity. Hence, throughout the experiments, the strips were used within 3 days after preparation. It was observed, however, that the strips kept in a polyethylene bag were sufficiently sensitive up to a month. The strips were not useful after three months.

In the present method, the chemicals commonly available in every laboratory have been used. Since acrylonitrile and ethylene oxide are inflammable, they are always used in mixture with non-flammable fumigants or carbon dioxide. These adjuvants have no effect on the color of the detector strip. Hence, the strip has the advantage of selectively detecting acrylonitrile and/or ethylene oxide fumigants in air and foodstuffs.

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Table 2. Desorbed residues of acrylonitrile and ethylene oxide in different foodstuffs detected by the detector strip method and estimated by GLC.

Foodstuffs	Moisture content (%)	Acrylonitrile		Ethylene oxide	
		Average residue estimated by GLC (ppm)	Detector strip color*	Average residue estimated by GLC (ppm)	Detector strip color*
Paddy	9.8	0.24	9B2, 9B2	0.92	9B2, 41D2
Polished raw rice	10.0	8.15	41F5, 41F5	3.49	41D2, 41D2
Wheat	12.1	7.58	41E3, 41E3	2.07	41D2, 41D2
Semolina	12.9	1.68	41C1, 41D1	0.73	41B1, 41D1
Split chickpeas	13.0	0.20	9B2, 9B2	0	9B2, 9B2
Curry powder	9.6	1.24	9B2, 9B2	0	9B2, 9B2
Peanuts	5.6	5.45	41D2, 41E3	0.92	41C2, 41D2
Dry Dates	9.2	3.15	41E3, 41F4	0.19	9A3, 9B2
Controls	-	0	9B2	0	9B2

* as read in the Dictionary of Color (MAERZ & REA PAUL 1950).

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