Trapping and Analysis of Atmospheric Residues of 2, 4-D

Eugene R. Johnson, Te C. Yu, and Marvin L. Montgomery
Department of Agricultural Chemistry
Oregon State University
Corvallis, Ore.

As part of a monitoring study to measure atmospheric residues of 2,4-D (2,4-dichlorophenoxyacetic acid), it was necessary to develop a method for trapping and analysis of low levels of herbicide. The two requirements of the method were that the system be capable of handling relatively large flow rates of air, and that the various derivatives of 2,4-D maintain their integrity in the trapping medium.

Large flow rates of air and handling of traps are more difficult with liquid absorbers. Thus it was desirable to use a solid adsorber. In surveying the literature it was noted that resins were effective in removing organic compounds from water (JUNK et al. 1974) and air (THOMAS and SEIBER 1974). Tests with XAD-2 showed this resin was an efficient 2,4-D adsorber, so an air sampling technique was developed using this material.

XAD-2 resin was purchased from Rohm and Haas (Philadelphia, PA). Salts and fine particles were removed by washing the resin beads with warm water in a 4 l beaker covered with a 35 mesh screen. The fines were floated out through the screen by tilting the beaker and introducing a stream of water down the lip of the beaker. Extraneous organic materials were removed by a 24 hour soxhlet extraction with distilled acetone. After drying at 30°C, the resin was ready for use.

Two types of air-sampling devices were assembled. The first was a small tube designed for continuous use at a fixed station. This trap was made from a 20 x 125 mm screw-cap culture tube. A 12/5 ball joint was fused to the bottom of the tube. A ball joint was used to facilitate changing tubes at the end of the sampling periods. These tubes were charged with 5 g of resin contained between two glass wool plugs. When in use, the tubes were clamped in an upright position and connected to the vacuum pump through use of thick-walled rubber tubing containing a 12/5 socket joint. Flow rates (about 10 l/minute) were controlled by placing a limiting orifice on the inlet side of the pump. After use, the screw-caps were put on the tubes to prevent contamination by extraneous materials. The sampler is shown in Figure 1.

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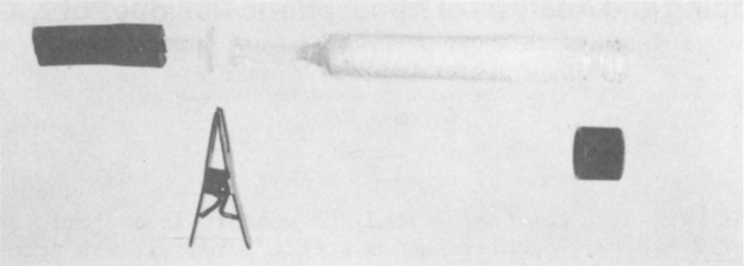

Figure 1. 2,4-D air sampling tube

The second sampler was designed for use with a portable, battery-powered pump. Since this system was restricted to shorter sampling periods (up to 1 hour), larger flow rates (50 l/minute) were required to give good sensitivity. Thus larger tubes were employed. The portable traps were 27 mm x 40 cm pyrex tubes into which an extra coarse fritted glass disc was fused. The bottom of the tube was drawn out so that it could be connected to the pump with 2 cm tygon tubing. The tube was charged with 15 g of resin held in place with a glass wool plug.

Most commercially available pumps are satisfactory for fixed station sampling. The only requirements are that a power outlet be available and the pump be capable of drawing in excess of 10 l/minute. Since portable units aren't readily available, a unit was assembled for use with a 12V storage battery. The unit consisted of a 1/4 HP DC motor coupled to a rotary vane vacuum pump. The unit was mounted in 20 x 20 x 50 cm box. The flow rate was controlled by a bleed valve connected to a flow meter which was mounted to the pump. This unit was used to take air samples at various altitudes from an airplane.

In the monitoring program we were concerned with the various 2,4-D formulations which might be used--esters, amines, acid. The esters on which we did recovery studies were the isobutyl, butyl, isooctyl, 2-ethylhexyl, butoxyethyl (BE), and propyleneglycolbutylether ester (PGBE). Recovery studies were run on the non-volatile acid and dimethylamine salt forms of 2,4-D.

In determining efficiency of absorption and extraction, 0.1 ml of a hexane solution of esters was placed in an L shaped side arm inserted in the top of the sampler tube. Care was taken to prevent solution from going directly on the resin. Air was drawn through the system for several days to volatilize the chemical onto the resin. Since the acid and amine forms are non-volatile, they were placed directly on the resin in 0.1 ml of acetone. Again, air was drawn through the tube for several days.

In extracting the resin, a teflon stopcock having a 12/5 socket joint on the top was connected to the bottom of the sampling tubes. After filling the tubes with nanograde hexane, the resin was stirred to release entrapped air and allowed to stand several minutes before opening the stopcock. The resin was extracted with 4 bed volumes of hexane, and the combined washes were boiled down to 10 ml on a steam bath. The L shaped side arm was also rinsed with hexane and the wash concentrated to 1 ml. The side arm washings were analyzed to determine if any ester had not volatilized.

The hexane extracts of field run samples were analyzed for 2,4-D by electron capture gas chromatography. If significant residues appeared or there were peaks which interfered with one of the esters, the extracts were subjected to silica gel cleanup. This was accomplished by passing a 5 ml aliquot of the extract through a 3 g sample of 60/200 mesh silica gel contained in a 1 cm chromatography column. After washing the column with successive 25 ml portions of 5% benzene in hexane and 25% benzene in hexane, the hydrocarbon esters (isobutyl, butyl, 2-ethyl hexyl and isooctyl) were eluted with 25 ml of 50% benzene in hexane. The butoxyethyl and PGBE esters were eluted with 75 ml of 80% benzene in hexane. Both eluates were concentrated to 10 ml and reanalyzed by electron capture GLC. Hexane extraction of the resin does not remove acid or amine forms of 2,4-D. Therefore, after drawing air through the tubes to evaporate residual hexane, the non-volatile forms of 2,4-D were extracted by washing the resin with 0.05 M NaOH in 50% ethanol. Again, 4 bed volumes of solvent were used. The alcohol was required to wet the hydrophobic resin. The combined alcohol extracts were concentrated to about 20 ml on a rotary evaporator and acidified with 50 ml of 0.1 M sulfuric acid. After extracting the 2,4-D with 2-20 ml portions of benzene, the extracts were transferred to a 50 ml screw-cap volumetric flask. After evaporation to dryness, the samples were ready for methylation.

Methylation was accomplished by adding 5 ml of 10% BF_3 in methanol, sealing the flask and heating for 1 hour on the steam bath. After cooling, 45 ml of water was added to destroy excess reagent, and 1 ml of benzene was added to extract methyl 2,4-D. Following vigorous shaking and separation of phases, the benzene extract was analyzed by microcoulometric GLC.

We emphasize the need for caution in using volumetric flasks for vacuum evaporation and heating under closed conditions. These procedures must be carried out in the fume hood. We thoroughly test all new flasks before use. Although we haven't had problems in evaporation, we have had new flasks rupture upon heating.

As noted earlier, the esters were analyzed on an EC detector while the methyl ester from the non-volatile forms was run on a microcoulometric detector. The column for separation of esters was 180 cm x 2 mm packed with 90 cm of 1% Carbowax 20 M on 60/80 Q. Analysis for all the esters in the unpurified samples was at 195°C. Following clean-up, the hydrocarbon esters were run at 195°C while the PGBE and butoxyethyl esters fraction was run at 210°C to sharpen up the peaks. The methyl ester was analyzed at 150°C on a 140 cm x 4 mm column packed with 6% OV-1 on 60/80 Gas Chrom Q.

RESULTS

In a series of seven recovery studies in which 5 µg of each ester was placed in side arm introduction tubes, absorption and extraction procedures were quite efficient. The average and range of recoveries of the respective esters were as follows: isobutyl, 95, 92-99, butyl, 94, 88-99, ethylhexyl, 94, 91-100, isooctyl, 96, 93-100, butoxyethyl, 86, 79-92, and propyleneglycolbutylether ester, 86, 79-92. These values include the amount of ester which did not volatilize. The unvolatilized ester ranged from 0 to 4%.

The relatively small amount of chemical which was not accounted for was either not extracted or was present as 2,4-D acid resulting from hydrolysis of ester on the resin. This conclusion was based on analysis of the alkaline alcohol extract of the ester-extracted resins. When the 2,4-D in this extract was added to the amount of ester found, the average recovery for all runs was 98%.

Similar results were obtained with the high-volume sampler tube. In a series of 3 day runs using 5 µg of each ester, over 90% recovery was obtained with each of the esters. The somewhat higher recoveries of the glycol esters (PGBE and butoxyethyl) with the high volume sampler may have been due to less hydrolysis because air was drawn through the tubes for shorter periods of time. The recovery of the acid and dimethylamine forms of 2,4-D was also quite good, with an average recovery of 97%.

The limits of sensitivity of these trapping and analysis procedures is about .01 µg/M^3 of 2,4-D using the small samplers and .05 µg/M^3 of 2,4-D using the larger tubes for the portable sampler. These values are based on a 24 hour sample at 10 l/minute for the small tubes and 50 l/minute for 1 hour with the larger tubes.

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