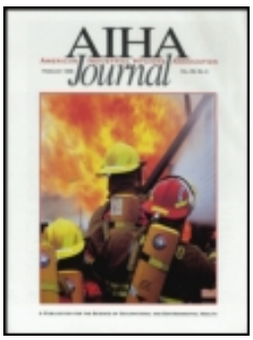

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A Sampling and Analytical Method for the Simultaneous Determination of Multiple Organonitrogen Pesticides in Air

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An air sampling and analytical method was developed for organonitrogen pesticides using a combined filter and XAD-2 sorbent sampler and high performance liquid chromatography-ultraviolet detection. The method was evaluated for 14 organonitrogen pesticides by National Institute for Occupational Safety and Health evaluation guidelines and procedures. Evaluation experiments addressed limits of detection and quantitation, analytical recovery, sampler capacity, sample stability, and precision and bias over a range of 12 to 240 μg per sample. Samples were stable when stored for up to 30 days under either ambient or refrigerated conditions. Based on the finding of this work, 10 of the 14 compounds studied (aldicarb, captan, carbaryl, carbofuran, chlorpropham, diuron, formetanate, methiocarb, oxamyl, propham) can be successfully determined simultaneously using one method with an accuracy of better than ±25% of the true value with 95% confidence. Two other compounds (carbendazim/benomyl, methomyl) can be measured with the same accuracy over a more limited concentration range. The remaining two compounds (propoxur, thiobencarb) may meet this criterion, but additional samples would need to be included in the data analysis. With the current data, these two compounds can be determined with an accuracy of better than ±27% of the true value with 95% confidence.

Keywords: pesticides, sampling

Evaluation of workplace chemical exposures for agricultural workers has received little attention in comparison with other occupations.[1] It also has been noted that lack of accurate exposure estimates has been a weak link in associations of pesticide exposures with occupational illnesses.[2] To address this need for accurate exposure estimates, more universal methods for pesticide monitoring have been developed.[3,4] The goal in this work was to provide methods that employ a universal sampler with analytical determinations designed for different classes of pesticides (e.g., organophosphorus, carbamate, etc.).

Previous work has shown the utility of the commercially available OSHA versatile sampler (OVS) tubes for the simultaneous determination of organophosphorus pesticides.[4] The comprehensive study described here examines the performance of this commercially available sampler (with quartz fiber filter) for the collection of organonitrogen-based pesticides. Method limits of detection and quantitation, desorption procedures and efficiencies, effects of temperature and humidity, media capacity, long-term stability of pesticides on the media and in solution, and precision and accuracy were studied using 12 carbamates, 1 substituted urea, and 1 sulfenimide. Established National Institute for Occupational Safety and Health (NIOSH) evaluation criteria were used to determine acceptance or failure of the method for each compound tested.[5–8] Selection of these 14 compounds involved consideration of toxicity,[9,10] frequency of requested analysis, availability of exposure limit values,[11,12] and production and usage volume.

Mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention.

MATERIALS AND METHODS

Reagents and Materials

Table I lists the pesticides selected for use in method development experiments. All pesticides were purchased from Chem Service Inc. (West Chester, Pa.) and were used without further purification (typically 97–99% pure). Acetanilide and acetophenone (Aldrich Chemical, Milwaukee, Wis.) were used as internal standards. Acetophenone was used as an internal standard for the 200-nm wavelength, and acetanilide was used for the 225-nm wavelength. Two internal standards were used because an occasional interference was observed at the retention time of acetanilide that absorbed strongly at 200 nm but not at 225 nm.

TABLE I. Pesticides Used in this Study

Compound	CAS #[A]	Toxicity Class[B]	PEL, REL mg/m³	Conc. Range (mg/sample)	Primary Use[B]
Aldicarb	116-06-3	I	n/a	0.012 – 0.24	insecticide
Benomyl	17804-35-2	IV	5.0	0.012 – 0.24	fungicide
Captan	133-06-2	I	5.0	0.048 – 0.96	fungicide
Carbaryl	63-25-2	I-IV	5.0	0.012 – 0.24	insecticide
Carbofuran	1563-66-2	I,II	0.1	0.012 – 0.24	insecticide
Chlorpropham	101-21-3	III	n/a	0.012 – 0.24	herbicide
Diuron	330-54-1	III	10.0	0.012 – 0.24	herbicide
Formetanate	23422-53-9	I	n/a	0.012 – 0.24	acaricide
Methiocarb	2032-65-7	I	n/a	0.012 – 0.24	insecticide
Methomyl	16752-77-5	I	2.5	0.012 – 0.24	insecticide
Oxamyl	23135-22-0	I	n/a	0.012 – 0.24	insecticide
Propham	122-42-9	IV	n/a	0.012 – 0.24	herbicide
Propoxur	114-26-1	I-III	0.5	0.012 – 0.24	insecticide
Thiobencarb	28249-77-6	III	n/a	0.012 – 0.24	herbicide

Note: n/a = no OSHA permissible exposure limit, NIOSH recommended exposure limit, or American Conference of Governmental Industrial Hygienists' threshold limit value exists.
[A]Chemical Abstract Service registration number
[B]Source: *Farm Chemicals Handbook '96*. Willoughby, OH: Meister Publishing Co., 1996.

All solvents (acetonitrile, methanol, acetone, 1-propanol, methylene chloride) were pesticide-grade and obtained from Burdick & Jackson (Muskegon, Mich.). Materials used in the evaluation experiments for analyte recovery were obtained from Gelman Science (Ann Arbor, Mich.; 13-mm glass fiber filters), SKC, Inc. (Eighty Four, Pa.; 11-mm quartz fiber filters, black polyurethane foam plugs), and Alltech Associates, Inc. (Deerfield, Ill.; 20/60 mesh XAD-2 resin). These materials were used as obtained without further cleanup to check analyte recovery. Commercially available air sampling tubes (SKC, Inc., 226-58 OVS sampling tubes) were used in experiments that simulated actual sampling.

Preparation of Stock Pesticide Solutions

Each of the pesticide stock standard solutions was prepared to produce a concentration from 5 to 10 mg/mL, depending on the solubility of the pesticide. These solutions were stable for up to 30 days when stored at –12°C.

Due to apparent incompatibilities between certain pesticides and solvents (e.g., decomposition, solubility), the stock standard solutions of the pesticides were prepared using the following solvents: (1) Stock solutions of chlorpropham and diuron were prepared at a level of 5 mg/mL in acetonitrile; (2) stock solutions of propoxur, oxamyl, methomyl, aldicarb, carbofuran, carbaryl, methiocarb, propham, and thiobencarb were prepared at a level of 10 mg/mL in acetonitrile; (3) stock solutions of captan and benomyl were prepared at a level of 5 mg/mL in methylene chloride, due to limited solubility in acetonitrile (<1 mg/mL; benomyl was more stable in a chlorinated solvent according to literature reports[13–15] and was observed to decompose to carbendazim); and (4) a stock solution of formetanate was prepared at a level of 5 mg/mL in 50/50 acetonitrile/methanol (v/v). Although formetanate broke down in pure methanol, some methanol was required to dissolve it at 5 mg/mL. When the solution was kept cold (–12°C), it did not break down during the study period.

Working standard mixtures were prepared in acetonitrile by combining stock solutions such that the concentrations of the pesticides in the working standard mixture were 120–400 µg/mL for each pesticide except captan, which was 480–1600 µg/mL. Further dilutions of these standards with acetonitrile were prepared as calibration standards. A small aliquot of 0.1 M triethylamine phosphate preservative solution (2 µL/mL solution) was added to the dilutions to help prevent decomposition of the combined analytes at room temperature. When solutions were stored at –14°C, addition of the preservative was not necessary.

High Performance Liquid Chromatograph (HPLC) Analytical System and Data Collection

Samples and standards were analyzed on a Perkin Elmer ISS 200 LC Sample Processor, Series 200 LC Pump, and 235 C Diode Array Detector using a 3.9-mm i.d. × 300-mm-long Nova-Pak® C_{18} HPLC column. Dual detector wavelengths were 200 nm and 225 nm. The injection volume was 5 µL. Mobile Phase A was 2% (v/v) 1-propanol and 98% water with 0.02 M triethylamine phosphate buffer at pH 7.0 ± 1. Mobile Phase B was 2% (v/v) 1-propanol and 98% acetonitrile. The flow rate was 1.0 mL/min. A solvent program provided a linear mixture change from 3% mobile Phase B through 95% B in 30 min with a 5-min hold at 95% B at the end. Postrun re-equilibration time was 15 min. A Waters Nova-Pak C_{18} guard column was used. The dwell volume was approximately 0.7 mL; this was equivalent to a 0.7-min solvent program delay at the beginning of each analytical run.

Sample Preparation and Analysis

Spiked samples were prepared using OVS-2 sampling tubes. The positions of the Teflon® retaining rings and filters were exchanged in the sampling tubes to prevent the spiking solution from wicking into the XAD-2 resin bed. Tubes were spiked in 10- to 15-µL aliquots at approximately 1-min intervals until the appropriate amount of analyte was fortified onto the sampling tube. Air was drawn through the tubes during spiking to help evaporate the solvent.

After spiking, conditioned air was pulled through the tubes at 1 L/min for a specified duration, depending on the experiment. At the end of a sampling period, the tubes were removed from the chamber. Each sampling tube was divided into three parts: Part A included the 270-mg XAD-2 front section, the quartz fiber filter, and the retaining ring from the OVS tube; Part B included the polyurethane foam divider and the 140-mg XAD-2 back section

from the same tube; Part C was a 1-mL acetonitrile rinse of inside walls of the empty sampling tube. Both 1 mL of desorption solvent (acetonitrile/0.2% (v/v) 0.1 M triethylamine phosphate buffer) containing 120 µg/mL of acetophenone and acetanilide, and 1 mL of 100% acetonitrile were added to Part A and Part B in separate 4-mL vials. One mL of desorption solvent was added to the tube rinse Part C in a third vial. All vials were tumbled for 1 hour, then filtered and transferred to analytical vials for HPLC analysis.

Sampling and Analytical Method Evaluation Protocol

After the chromatographic separation conditions for the analytes were defined and the analytical recovery of the analytes from the samplers verified, the method was evaluated according to NIOSH procedures.[5,6,8] The evaluation experiments included the determination of limits of detection and quantitation, sample capacity, storage stability, and precision and bias.

The generation of pesticide-containing aerosols was not attempted because of the physical nature of these compounds (e.g., low volatility) and limited generation capability. To simulate generated samples, OVS tubes were spiked with aliquots of pesticide-containing solutions, and humidified air at controlled temperature was pulled through each sampler to mimic the evaporative process that would occur during actual sampling. Temperature and humidity were maintained in the airstream using a previously described exposure chamber.[4] The amounts fortified on the tubes covered a range of 12 to 240 µg per sample except captan (48–960 µg per sample). Although pesticide aerosols were not generated, an experiment described in the Vapor Generation Study section was conducted to test the ability of the sampler to collect pesticide vapor.

Results and Discussion

An attempt was made to determine the target analytes by gas chromatography with nitrogen selective detection. Of 13 compounds studied (carbendazim/benomyl was excluded), only 6 compounds were detected with satisfactory peak shape for gas chromatography. Also, the limits of detection for these compounds would have been higher with this analysis approach. This information suggested that a liquid chromatography-based method for simultaneous determination of these compounds would be needed.

Many different liquid chromatographic conditions were investigated to provide for separation of all 14 compounds under study. Various mobile phases, gradient conditions, and injection volumes were investigated. Two detector wavelengths (200 and 225 nm) were selected to provide the best compromised response for O-aryl (λ_{max} 190–215 nm) and N-aryl (λ_{max} 205–235 nm) carbamate pesticides. Most of the pesticides were quantified at the 225-nm wavelength. Aldicarb and captan were quantified at the 200-nm wavelength to reduce noise in the detector response. The chromatographic separation obtained with the conditions listed in the Materials and Methods section are shown in Figures 1A and 1B. A re-equilibration time between runs of at least 15 min is necessary, or else erratic peak shapes and retention times will be observed in subsequent analyses.[16] Although baseline resolution was obtained for most of the compounds studied, interfering compounds may be present in field samples. If interferences are suspected in the analysis, the identification of the pesticide should be confirmed by analysis on an alternate column or under different elution conditions.

Stability of carbaryl and methiocarb was a problem when they were diluted in acetonitrile as working standards, so many different additives were tried to help stabilize these compounds in solution. The stability problem was solved by addition of a small amount of the triethylamine phosphate preservative solution (2 µL per mL of acetonitrile) to the analyte-containing solution. Because of this finding, the desorption solvent used to recover the analytes from the samplers was acetonitrile with 0.2% (v/v) 0.1 M triethylamine phosphate buffer.

Recovery of the pesticides from individual sections of the sampler was studied to see whether the sections could be combined for analysis. In addition, both glass fiber and quartz fiber filters were evaluated for recovery and found to perform equivalently. Recovery of all 14 analytes from the quartz fiber filters over the range of 12–240 µg/sample was 96.6 to 102%. Since quartz fiber filters were found to give better recoveries for the organophosphorus pesticides in a previous study,[4] quartz fiber filters were used in the remainder of the samplers in this study. For the polyurethane plugs, recovery ranged from 98.4 to 103.3% for all compounds except formetanate (85%). Recovery from the XAD-2 sorbent ranged from 95.2 to 103.6%, except for thiobencarb (87.4%) and benomyl/carbendazim (91.8%). The lower

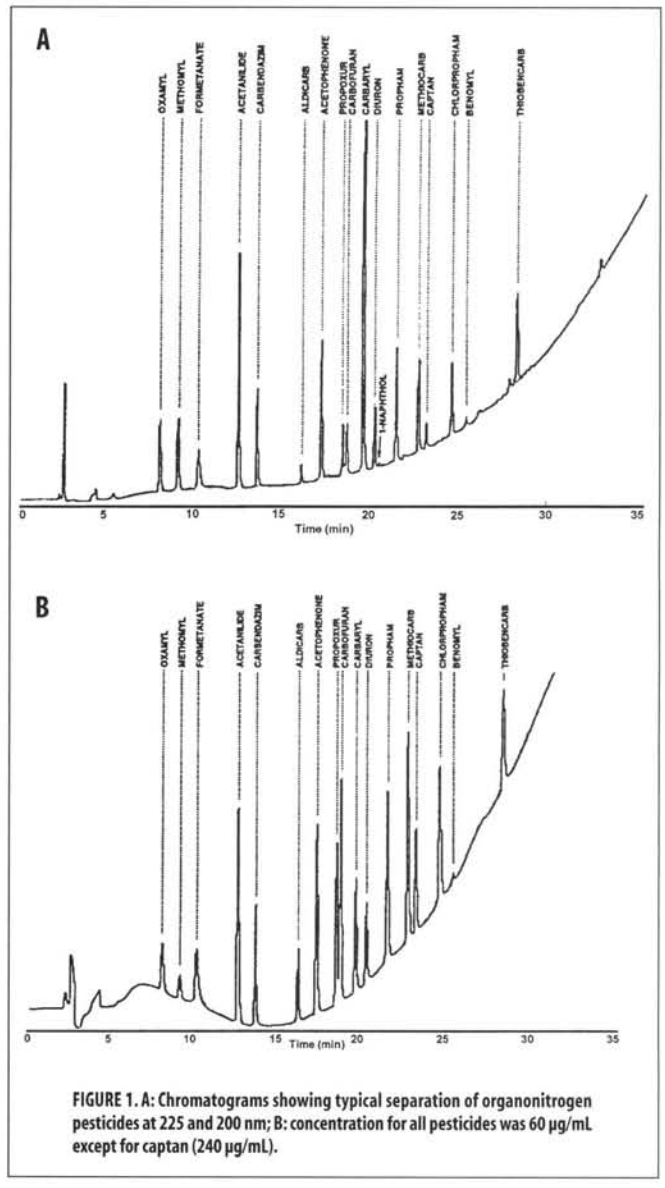

FIGURE 1. A: Chromatograms showing typical separation of organonitrogen pesticides at 225 and 200 nm; B: concentration for all pesticides was 60 µg/mL except for captan (240 µg/mL).

recovery from XAD-2 of thiobencarb (87.4%) might be due to its lower polarity, and therefore greater affinity for the nonpolar XAD-2 resin. These results show that in most situations, the filter and front sorbent section can be combined for desorption of the sampler. In situations where only benomyl/carbendazim or thiobencarb is present, the separate desorption of the filter and XAD-2 resin may be warranted.

Sampling and Analytical Method Evaluation

Since this method might be used in work environments with temperature and humidity extremes, these factors were included in the evaluation of the method. To ensure that the effects of temperature and relative humidity (RH) would not alter analyte recovery, triplicate samples at each of four concentrations were prepared and weathered under four different sets of temperature and RH (30°C and 80% RH; 30°C and 15% RH; 10°C and 15% RH; 10°C and 80% RH). Overall average recoveries at all four sets of conditions were not different (92.3–105% recovery). Based on these findings, the method is considered insensitive to temperature and RH effects. The remainder of the studies were carried out at conditions of 22–24°C and 10–40% RH, since these were the easiest conditions to maintain in the generation system.

To evaluate the capacity of the OVS sampler, the filters of 12 samplers were fortified with 480 µg of each pesticide. Fortified tubes were weathered for 2-, 4-, 6-, 8-, 10- and 12-hour sampling periods at a known temperature, humidity, and a flow rate of 1 L/min. Since breakthrough of the analytes was to be determined, only the backup section of each sampling tube was analyzed and compared with the total amount of fortified analyte to determine whether there had been breakthrough. The backup section was removed without disturbing the front section to avoid cross-contamination. No pesticides were detected at a level greater than the detection limit in any sampler tube for any weathering time. This finding shows that the sampler capacity was not reached in this experiment. According to the NIOSH guidelines,[8] the time to reach breakthrough is multiplied by a safety factor of 0.667. Since that breakthrough did not occur after 12 hours, there should be no difficulty in sampling for a maximum time of 8 hours.

Typically, samples should be stable over a period of 7 days at ambient temperatures for shipment back to the laboratory. Once the samples were at the laboratory, analysis could be delayed for up to 30 days. To ensure the stability of the OVS-2 tubes over a 30-day period, 49 samplers were spiked with 60 µg of each pesticide per tube except captan (240 µg), weathered for 4 hours, and stored at ambient and refrigerated temperatures (22–24°C and –12°C ± 1°C). Samples were analyzed on Day 0 (seven samples), Day 7 (seven samples at refrigerated temperatures; seven at ambient), Days 10, 14, 21, and 30 (three samples for each day at refrigerated temperatures; four at ambient).

The analysis data showed no loss of analyte beyond 10% of the Day 0 analysis results for the ambient samples. The recoveries of all analytes ranged from 90–100% for Day 0 analyses to 94–95% for Day 30 analyses. No difference in recovery between refrigerated and ambient storage conditions was observed. Based on these results, the analytes were stable after collection for 30 days. Although the experiment did not indicate that refrigeration of the samples was necessary, in certain instances minor improvements in the recovery at the 21-day and 30-day storage times (typically 1–2%) were noted. Therefore, refrigeration of samples after return to the laboratory for analysis is recommended for optimal recovery after storage.

Method precision and accuracy were determined by fortifying 28 tubes at 4 different concentration levels (7 tubes at the 12-, 60-, 120-, and 240-µg levels for each pesticide except captan [captan was fortified at 4 times these amounts] and weathering them for 4 hours at 40% RH and 24°C). Recoveries were calculated based on the original spike after desorption efficiency correction. For each set of samples, the recoveries were averaged and the standard deviation was determined. Most of the average recoveries (desorption efficiency corrected) are greater than 90% with precisions (S_r) of less than 7%. Bias ranged from a high of +5% to a low of –6%. The recovery data for both carbendazim and thiobencarb (–6% bias) were low but still acceptable. A plausible explanation for the low recoveries and higher standard deviations for carbendazim is that it is a breakdown product of benomyl and could be further broken down to other compounds. The low recoveries of thiobencarb can be attributed to the difficulty of removing the analyte from the resin due to its low polarity and the high polarity of the extraction solvent. The accuracy of the method for all compounds, based on a point estimate,[7] ranged from 17 to 20%, with only carbendazim at 27.8%. Ten of the 14 compounds met the NIOSH accuracy criterion of 25% with 95% confidence for all 4 concentration levels investigated. The calculated accuracy data are shown in Table II. In two cases (methomyl and carbendazim), the method met the NIOSH accuracy criterion if the upper concentration levels were

TABLE II. Organonitrogen Pesticide Method Summary

Compound	Number of Samples	S_{rt}[A]	Bias	Accuracy[B]	$A^{0.05}$[C]	$A^{0.95}$[D]
Aldicarb	28	0.066	–0.009	0.181	0.142	0.226
Captan	28	0.061	–0.036	0.179	0.143	0.222
Carbaryl	28	0.061	0.012	0.177	0.141	0.220
Carbendazim	28	0.112	–0.068	0.278	0.209	0.362
Carbendazim	21[E]	0.061	0.006	0.174	0.135	0.224
Carbofuran	28	0.060	–0.020	0.171	0.137	0.212
Chlorpropham	28	0.068	–0.017	0.184	0.145	0.232
Diuron	28	0.060	–0.062	0.192	0.156	0.235
Formetanate	28	0.056	0.032	0.179	0.145	0.220
Methiocarb	28	0.061	0.009	0.175	0.140	0.217
Methomyl	28	0.076	–0.002	0.200	0.154	0.256
Methomyl	21[E]	0.063	–0.002	0.176	0.136	0.228
Oxamyl	28	0.055	0.037	0.181	0.147	0.222
Propham	28	0.066	–0.053	0.195	0.156	0.243
Propoxur	28	0.079	0.007	0.207	0.159	0.265
Thiobencarb	28	0.073	–0.068	0.214	0.171	0.268

[A]Pooled method precision
[B]Calculated method accuracy
[C]Lower 5% confidence limit on method accuracy. If this value exceeds 0.25, the method will not meet the NIOSH accuracy criterion.
[D]Upper 95% confidence limit on method accuracy. If this value exceeds 0.25, the method may not meet the NIOSH accuracy criterion.
[E]This method meets the NIOSH accuracy criterion only for the lower three concentration levels.

removed from the data reduction. The data for carbendazim at the highest concentration had worse precision and lower recovery than the other three lower concentration levels. For methomyl, the data for the highest concentration level had the worst precision value of the four concentration levels. In the other two cases with propoxur and thiobencarb, where the compounds may not meet the NIOSH accuracy criterion, additional samples would be needed to make this determination. It was noted that the tail of the chromatographic peak for propoxur overlapped with carbofuran and may not have been integrated properly, causing elevated precision values. Since the upper 95% confidence limits on the accuracy estimate were only slightly above 26%, the method should fulfill the NIOSH accuracy criterion for these two compounds.

NIOSH Standard Operating Procedure (SOP) 018[8] was used to determine limits of detection (LOD) and limits of quantitation (LOQ) using a linear fit of data and the lowest four sets of standards (analyzed in triplicate). Except for propham and captan, the LODs calculated for the analytes were below the lowest standard. According to SOP 018 the lowest standard is reported as the LOD (0.6 µg/sample; 0.06 µg/sample for carbaryl). For propham and captan, the LODs were 0.8 and 3.3 µg/sample, respectively. The LOQ values ranged from 0.08 µg/sample for carbaryl to 11 µg/sample for captan. Typical LOQ values were 2.0 µg/sample for the other compounds except for aldicarb (2.42 µg/sample) and propham (2.35 µg/sample).

Vapor Generation Study

To verify the ability of the sampler to collect pesticide vapors, a method similar to that of Roper et al.[17] was used to generate vapors. The "generator" tube was an empty OVS tube fitted with a small plug of fused silica wool at the narrow-necked end. With the open wide-mouthed end of each generator tube facing the open wide-mouthed end of the sampler OVS tube, the two tubes were taped together with Teflon tape (see Figure 2). The combined tube assemblies were then inverted so that the inlet end (i.e., the narrow end of the generator tube) faced downward. The narrow end of the OVS-2 sampler tube faced upward and was attached to a vacuum source maintained at a flow of 0.2 L/min controlled by a critical orifice needle. As the air was being drawn into the tube assembly, identical 0.3-mL aliquots of working standard mixtures were spiked through the narrow neck of the generator tubes onto the quartz wool. The inverted orientation prevented the liquid spiking solution from running down onto the quartz fiber filter of the sampler OVS-2 tube until the solvent evaporated from the quartz wool. Also, the upward airflow prevented the spiking solution from running through the quartz wool in the neck of the generator tubes.

After the solvent was evaporated to dryness, each assembly was transferred to a port in the environmental chamber. Under the selected conditions for weathering, seven of these assemblies were weathered for 7 hours with air drawn through the device at 1 L/min. At the end of the sampling period, the assemblies were removed from the chamber and the generator tubes were separated from the sampler tubes.

Most of the mass of each compound was usually found in the generator tubes. In Table III the average of the recoveries is given for the samplers and the generator tubes. The total of the sampler and generator values in Table III shows nearly quantitative recovery (>90%) of each analyte, except for formetanate (61.3%) and thiobencarb (86.0%). Benomyl was recovered from the generator tube at only 11.3%, but it converted to carbendazim. Although the combined benomyl and carbendazim results are high (126.5%), the data for benomyl are insignificant for showing trapping efficiency since both benomyl and its breakdown product, carbendazim, remained in the generator tube, as did oxamyl and formetanate. These four analytes were not anticipated to volatilize, considering their basic nitrogen groups and/or multiple polar functional groups. However, the volatility of diuron (4.2% evaporated) was not anticipated. These values were not corrected for desorption efficiency of the quartz wool, which was assumed to be 100%.

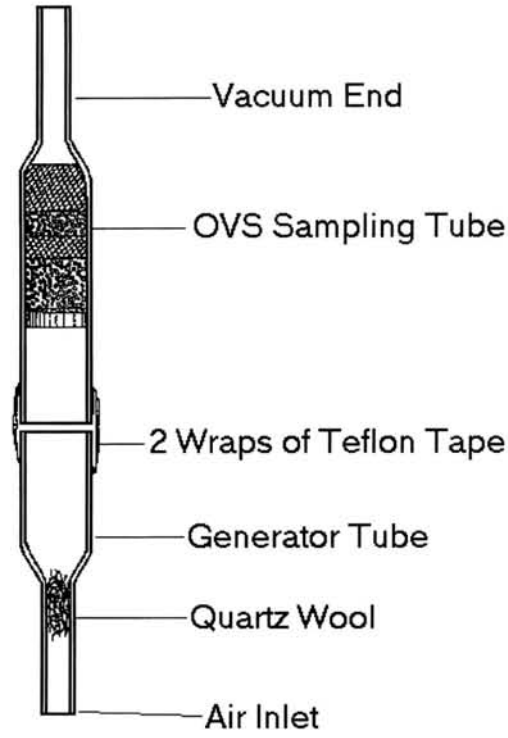

FIGURE 2. Generator tube and OVS tube assembly used for vapor phase generation experiment

TABLE III. Generated Samples—Percentage Collected on Individual Tubes

Analyte	Average % (Sampler)	Average % (Generator)	Total %[A]
Aldicarb	79.5	13.8	93.3
Benomyl	0.0	11.3	11.3
Captan	15.3	79.3	94.6
Carbaryl	15.0	81.9	96.8
Carbendazim	0.0	115.0	115.0
Carbofuran	38.6	55.1	93.8
Chlorpropham	73.0	18.2	91.2
Diuron	4.2	94.4	98.6
Formetanate	0.0	61.3	61.3
Methiocarb	20.5	76.3	96.8
Methomyl	45.4	50.3	95.6
Oxamyl	0.0	94.9	94.9
Propham	91.2	2.5	93.7
Propoxur	69.9	24.7	94.6
Thiobencarb	58.3	27.7	86.0

[A]Based on seven replicates

CONCLUSIONS

A sampling and analytical method for the simultaneous determination of 14 organonitrogen pesticides was developed and evaluated. Samples were collected with OVS air sampling tubes, desorbed with 2 mL of acetonitrile/0.2% (v/v) triethylamine phosphate buffer, and analyzed by HPLC with dual wavelength detection. Based on this research, at least 10 of these 14 compounds can be determined over a range of 12 to 240 µg per sample with an accuracy of ±25% with 95% confidence. Two other compounds will meet this criterion over the range of 12 to 120 µg. This method will be included in a future supplement to the fourth edition of the *NIOSH Manual of Analytical Methods as Method 5601*, Organonitrogen Pesticides.

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