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Development of analytical methods for agricultural chemicals

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The goal of this research was to develop several sampling and analytical methods for different classes of agricultural chemicals in air. Most sampling methods for pesticides have used a sampler that is a combination of a filter and a secondary medium (1, 2). To provide a convenient sampler for compounds which may exist in air as both aerosols and vapors, researchers at the Occupational Safety and Health Administration (OSHA) developed the combined filter/sorbent tube sampler shown in figure 1, known as the OSHA versatile sampler (OVS). The OVS was commercially available and compact, it collected both aerosol and vapor, and it had been tested by researchers at OSHA for several individual pesticides (3). When a universal sampler for agricultural chemicals was required, NIOSH researchers felt that the OVS sampler was a logical choice. Although sampling and analytical methods for several different pesticide classes were proposed for development with the use of this sampler, time and financial restrictions allowed the development of only one method for organophosphorus pesticides with the use of gas chromatography-flame photometric detection (GC-FPD). The selection of the organophosphorus compounds to be included in the method was based on their toxicity, commercial use, and exposure limit values (NIOSH recommended exposure limits, OSHA permissible exposure limits, American Conference of Governmental Industrial Hygienists' threshold limit values).

Evaluation protocol for the sampling and analytical method

The evaluation of the sampling and analytical method was based on the method evaluation protocol of the joint OSHA-NIOSH Standards Completion Program (4). The primary objective of this method evaluation research was to determine if the method met an accuracy criterion that required 95% confidence that the inaccuracy of the method was no more than ±25% of the true amount measured with a probability of 0.95. Additional parameters of this sampling and analytical method were evaluated through the experiments defined in the protocol. These experiments included the evaluation of the desorption efficiency, sample capacity, sample stability, and precision and accuracy. Some of the experiments in the protocol address long-term sample stability (30-d storage), overnight sample preparation and storage prior to analysis, short-term exposure limits, and concentration levels down to 0.1 times the exposure limit.

The generation of pesticide-containing aerosol and vapor atmospheres for this research effort was not attempted due to the physical nature of these compounds and resource limitations. To simulate generated samples, OVS tubes were fortified with aliquots of analyte dissolved in toluene, and humidified air was pulled through each sampler to mimic the evaporative process that occurs during actual sampling. If the analyte had a ceiling or short-term exposure limit, the amount of analyte added to the sampler was adjusted for the shorter sampling time required at this exposure limit.

Desorption efficiency. The filters and front sorbent beds of sets of six samplers were fortified separately, a syringe being used to inject a standard solution of pesticides onto the sampling media. The media were fortified with amounts of analyte equivalent to sampling concentrations of 0.1, 0.5, 1.0, and 2.0 times the exposure limit for a minimum of 4 h at 1 $l \cdot min^{-1}$. Backup sections of the sorbent beds were fortified with amounts of analyte equivalent to 25% of the amount fortified on the front sections of the samplers. To be considered an acceptable method, recoveries from the filters and front sections of the medium were required

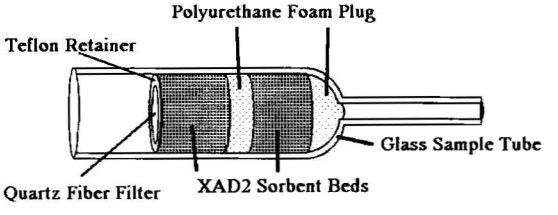

Figure 1. Diagram of the OSHA versatile sampler (OVS), showing the incorporated modifications. (OSHA = Occupational Safety and Health Administration)

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to be greater than 75% for levels equivalent to sampling 0.5, 1.0, and 2.0 times the exposure limit. Recovery from the backup section of the sampler was noted so that appropriate recovery corrections could be applied if breakthrough occurred during the sampling.

Capacity of medium and maximum recommended sampling time. Samplers were fortified with the amount of analyte which would be collected by sampling an atmosphere of two times the exposure limit for 8 h at a flow rate of 1 $l \cdot min^{-1}$. Clean, humidified air was drawn through the sampler at this flow rate for up to 12 h. When the amount of the analyte in the integrated effluent of the sampler exceeded 5% of the amount fortified on the filter, the capacity of the sampling medium had been reached. The time at which this point was reached was the breakthrough time at the given sampling rate. To find the maximum recommended sampling time, the breakthrough time was multiplied by 0.667. If breakthrough was not detected after 12 h, a maximum recommended sampling time of 8 h was used. If the capacity of the sampler was not sufficient to allow a reasonable sampling time, a lower flow rate was used for this capacity study.

Sample stability. Twenty-four samplers were fortified with an amount of analyte equivalent to sampling a concentration of 0.5 times the exposure limit for a minimum of one-half the recommended sampling time. Clean, humidified air was sampled through the samplers for half of the maximum recommended sampling time at the recommended flow rate. The samplers were divided into two groups of six and four groups of three, one group of six being analyzed as soon as possible. The remaining group of six was stored at ambient temperature and analyzed after 7 d. The other 12 samplers were stored under refrigeration and analyzed in groups of three at 10, 14, 21, and 30 d after fortification. If the mean recovery of the group of six samplers analyzed on day 7 differed from the day 1 results by more than 10%, the samples were deemed unstable, and the method did not meet the stability requirement for that particular analyte. If a plot of recovery versus time showed that recovery decreased by more than 10%, the samples were considered to be stable for the number of days for which the recovery was >90%.

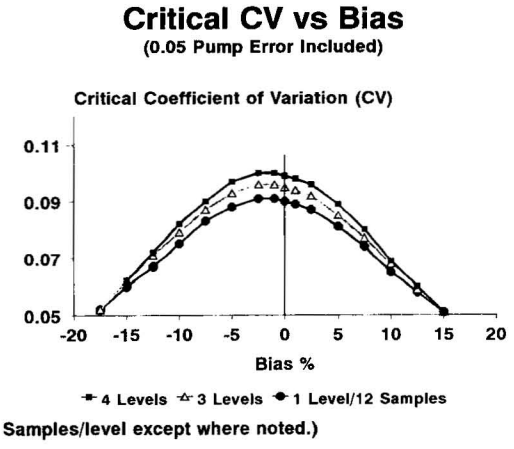

Figure 2. Graph of critical coefficients of variation versus bias. This graph covers three and four levels of concentration. One level of concentration is included for short-term samples (12 samples).

Precision and accuracy. Sets of six samplers were fortified with amounts of analyte equivalent to sampling concentrations of 0.1, 1.0, and 2.0 times the exposure limit for a minimum of 4 h at a flow rate of 1 $l \cdot min^{-1}$. If the analyte had a ceiling or short-term exposure limit, an additional set of 12 samplers was fortified at this exposure limit. Clean, humidified air was sampled through the samplers for half of the maximum recommended sampling time at 1 $l \cdot min^{-1}$. The coefficient of variation (CV) of the samples (pooled from the CV of the filter and front sorbent bed) at each concentration level was calculated, and the homogeneity of these values was checked with Bartlett's test (5). If the CV values were not homogeneous, the sample set collected at 0.1 times the exposure limit was removed, and Bartlett's test was recalculated. The pooled CV for the unbiased results of three groups of six samplers collected under this experiment and the group of six samplers collected under the sample stability experiment (analyzed as soon as possible) was required to be ≤ 0.099 for the method to meet the aforementioned accuracy criterion. If the pooled CV exceeded 0.099, then the set of samples collected at 0.1 times the exposure limit was excluded to determine if the method would then meet the accuracy criterion. For the measurements with short-term exposure limits, the CV for the unbiased results of 12 samplers was required to be <0.09 to meet the accuracy criterion. For methods with a defined bias, figure 2 shows the CV that must be achieved to meet the accuracy criterion. Estimated bias, based on the amount of material fortified on the samplers, should be less than 10% to meet the accuracy criterion.

Sampling and analytical method

Nineteen organophosphorus pesticides were investigated with the use of GC-FPD. These compounds were azinphos-methyl, chlorpyrifos (Dursban), diazinon, dicrotophos, disulfoton (Di-Syston), ethion, ethoprop (MOCAP), fenaminphos, fonofos, malathion, methamidophos, methyl parathion, mevinphos (Phosdrin), monocrotophos, fenchlorphos, parathion, phorate,

sulprofos, and terbufos (Counter). Preliminary desorption studies with the 19 compounds revealed that some of the compounds were not stable on the glass fiber filters. Quartz fiber filters were found to provide stable recoveries for all of the compounds. From this point on, all of the samplers used the quartz fiber filters. Desorption of the compounds from both the filter and sorbent were optimized with the use of 10% acetone in toluene. Recovery was greater than 80% for all of the compounds studied.

None of the 19 compounds exhibited breakthrough into the backup sorbent bed, even after air was drawn at 1 $l \cdot min^{-1}$ through the samplers for 12 h. All of the compounds were stable on the sampler for 30 d. The overall CV values for all of the analytes ranged from 0.063 to 0.071. On the basis of this research, all of the compounds can be determined over the range of 0.1 to 2 times the exposure limit with an accuracy of ±25% of the true value 95 times out of 100. This method will be included in the 4th edition of the *NIOSH Manual of Analytical Methods.*

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