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DETERMINATION OF 2,4-DICHLOROPHENOXYACETIC ACID IN SOILS BY CAPILLARY GAS CHROMATOGRAPHY WITH ION-MOBILITY DETECTION

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SUMMARY

A simplified procedure for quantifying 2,4-dichlorophenoxyacetic acid (2,4-D) residues in soils has been developed. Soil samples are extracted, esterified with methanol in the presence of a boron trifluoride catalyst and analyzed by capillary gas chromatography without further time-consuming cleanup steps. The success of the procedure depends on substituting a tunable selective ion-mobility detector for the commonly used electron-capture detector. By selectively monitoring the product ion formed when the methyl ester of 2,4-D undergoes electron capture, the ion-mobility detector can detect 2,4-D in the presence of other electron-capturing compounds. A recovery of 93 % of 2,4-D at the 50 ppb level in spiked soils is achieved.

INTRODUCTION

Quantifying organic compounds present at or below the parts per million level in complex environmental samples is often difficult. A number of analytical steps may be required to extract the species of interest from the sample matrix, isolate it from potentially interfering compounds and unambiguously establish its concentration. For those chemicals which are volatile, either naturally or following suitable derivatization procedures, capillary gas chromatography (GC) with the wide range of selective detectors available is frequently the analytical method chosen to perform final separation and quantification steps. Despite the power of this technique, however, pre-chromatography cleanup procedures are often necessary owing to the complexity of the sample. A case in point is the determination of organochlorine herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D) and related compounds in soils.

2,4-D is commonly used, both in agriculture and by home-owners, for the control of broadleaf weeds. Even though it is applied as a post-emergence treatment, a significant portion of this herbicide may be transferred to the soil, where it becomes subject to migration by water runoff and degradation by biological processes. A number of investigations have shown that degradation of 2,4-D in soils is generally rapid[1–4] with little of the intact herbicide being incorporated into humic and fulvic acid materials on a long-term basis[5]. Nevertheless, monitoring of 2,4-D residues in soils remains important for purposes of charting migration from treated to non-

treated lands, determining contamination from aerial drift of herbicide sprays during application and estimation of exposure hazards to agricultural workers.

Chlorophenoxyacetic acid herbicides may be extracted from soils in a number of ways. Acidification of the soil sample followed by extraction with diethyl ether[6] and extraction with saturated aqueous calcium hydroxide[7] have both been shown to be effective. Procedures recommended by the U.S. Environmental Protection Agency (EPA) for determination of organochlorine pesticides and herbicides in general rely on Soxhlet extraction of the soil sample with a 1:1 mixture of acetone and hexane after acidification with sulfuric acid[8]. A comparison of other common methods and extraction solvents has been provided by Woolson and Kearney[9]. Because 2,4-D cannot easily be chromatographed in its free acid form, soil extracts are invariably subjected to an esterification procedure prior to analysis by gas chromatography with electron-capture detection. Many appropriate procedures have been described, including reaction of the free acid with an alcohol in the presence of a Lewis acid catalyst such as boron trifluoride[10,11], diazoalkylation[6,10,12], ion-pair alkylation using iodoethane with tetrabutylammonium hydrogen sulfate counter ion[7] and mineral acid-catalyzed reaction with alkyl alcohols[10]. Halogenated esters have also been prepared to increase the response sensitivity in the electron-capture detector[13,14].

Soil samples prepared for GC analysis by any of the above procedures are likely to contain an abundance of organic compounds, many of which are electron-capturing. If any of these species are not well separated from the 2,4-D derivative of interest, quantification can be severely hampered. Therefore, an additional cleanup step by column chromatography with aluminum oxide and/or Florisil columns[6,8] is routinely employed to remove many interfering compounds prior to injection of the sample into a gas chromatograph. Although such procedures are effective in removing the bulk of impurities from the sample, they are time consuming and increase the potential for analyte loss owing to the number of manipulations involved. The use of a GC detector capable of monitoring 2,4-D esters selectively in the presence of other electron-capturing organic compounds, instead of the normally used electron-capture detector, would eliminate the need for column chromatographic cleanup of samples and thereby significantly simplify the analysis.

An alternative procedure for quantification of 2,4-D in soils has been developed in this laboratory, involving capillary gas chromatography with ion-mobility detection. The ion-mobility detector employed was constructed specifically as an atmospheric pressure tunable selective detector for gas chromatography and is closely related to a direct-current (d.c.) electron-capture detector. A 15 mCi nickel-63 foil in the detector ionization cell initiates a series of charge-transfer reactions which ultimately ionize organic compounds via mechanisms directly comparable to those occurring in the electron-capture detector[15]. Unlike a d.c. electron-capture detector, however, the ion-mobility detector accelerates product ions formed in these charge-transfer reactions down an ion drift tube with a uniform electric field gradient of typically 150–250 V/cm, where they are separated according to their mobilities at atmospheric pressure in a countercurrent flow of nitrogen. The detector may be easily tuned to monitor ions of a pre-selected mobility, resulting in the ability to detect selectively many compounds from among those responding universally in the standard electron-capture detector. Construction details, schematic diagrams and operating characteristics of this unique GC detector have been reported previously[16,17] and

will not be repeated here. The performance of the ion-mobility detector towards a number of halogenated compounds, including selective monitoring of chlorine- or bromine-containing species undergoing dissociative electron capture, has been evaluated[18]. In this paper a simplified procedure for quantifying 2,4-D residues in soils is presented, together with the analysis of samples drawn from a variety of agricultural areas.

EXPERIMENTAL

Apparatus

A Tracor 560 capillary gas chromatograph (Tracor Instruments, Austin, TX, U.S.A.), equipped with a split–splitless injector and a 15-m SE-54 fused-silica capillary column (J and W Scientific, Rancho Cordova, CA, U.S.A.) was used for all studies. The carrier gas (helium) flow-rate was 2 ml/min, the injection port temperature was 250°C and a 50:1 split injection was employed. The GC oven was temperature-programmed from 100 to 200°C at 10°C/min. Chromatograms obtained with flame-ionization or pulsed electron-capture detectors followed standard operating procedures recommended by the manufacturer.

The operating parameters of the ion-mobility detector were as follows: ion drift length, 7.5 cm; electric field gradient, −230 V/cm; temperature, 200°C; and pre-purified nitrogen drift gas flow-rate, 400 ml/min. An oxygen make-up gas flow-rate of 200 ml/min was used to increase the detector sensitivity. The ion-mobility detector is housed in a laboratory oven adjacent to the gas chromatograph for ease of accessibility. The capillary column was therefore routed through a heated, insulated transfer line, maintained at 200°C, to reach the detector.

Chemicals and reagents

2,4-Dichlorophenoxyacetic acid was obtained from Eastman-Kodak (Rochester, NY, U.S.A.). With the exception of acetone and hexane (Burdick & Jackson Labs., Muskegon, MI, U.S.A.) and boron trifluoride (Matheson, Secaucus, NJ, U.S.A.) all chemicals and reagents were purchased from J. T. Baker (Phillipsburg, NJ, U.S.A.). Ortho Weed-B-Gon (Chevron Chemical, Ortho Consumer Products Division, San Francisco, CA, U.S.A.) was chosen as a typical, readily obtainable source of 2,4-D for use in home gardens.

Extraction and esterification procedures

All soil samples were obtained by random grab sampling at the respective locations indicated in the figure captions. Because the purpose of these studies was to evaluate a new analytical procedure by means of the ion-mobility detector and not to provide an in-depth statistically valid survey of 2,4-D concentration at any one location, multiple samples at each site were not collected. The Chehalis, Washington soil, supplied by the Washington State University Department of Agronomy and Soils, was collected in 1932, long before 2,4-D became available for use in agriculture. This soil provided a blank and was used in recovery studies. The extraction procedure was carried out as follows. A 10-g air-dried soil sample was finely ground with a mortar and pestle, suspended in a minimum amount of deionized water and acidified (pH 2) with sulfuric acid to ensure that all 2,4-D was present in the acid form. The soil

was air-dried for 24 h before being Soxhlet-extracted for 6 h with 125 ml of acetone–hexane (1:1) according to EPA procedures[8]. The solvent was evaporated nearly to dryness on a rotary evaporator at room temperature and the residue was taken up in 5 ml of methanol.

Esterification to form the methyl ester of 2,4-D was carried out in the presence of boron trifluoride as a catalyst according to the procedure of Horner *et al.*[10]. Approximately 5 ml of the catalyst mixture (0.2 g of boron trifluoride per millilitre of methanol) was added to the soil extract and the resulting solution refluxed at 100°C for 15 min. Following removal of excess methanol by rotary evaporation, the catalyst was destroyed in water and the aqueous solution was extracted with diethyl ether (3 × 10 ml). The ether extracts were evaporated to approximately 0.1 ml at room temperature and made up to a known volume in methanol. Quantification by gas chromatography with the ion-mobility detector was undertaken without further cleanup.

The 2,4-dichlorophenoxyacetic acid standard was esterified by the same procedure. The purity of the ester was confirmed by gas chromatography, melting point determination and NMR spectroscopy. The ester was dissolved in methanol and used to produce a calibration graph for the ion-mobility detector.

To test the performance of this procedure on a different sample matrix, a dandelion was treated with Ortho Weed-B-Gon following the manufacturer's recommended procedure. After 48 h the weed was uprooted and a 25-g portion of the upper foliage was finely chopped in a blender. The resulting sample was extracted with deionized water (3 × 100 ml) and the extract was acidified (pH 2) with sulfuric acid. Organic compounds were extracted into diethyl ether (3 × 20 ml), the ether was evaporated nearly to dryness and the residue was taken up in methanol for esterification by the procedure outlined above.

RESULTS AND DISCUSSION

When the ion-mobility detector is configured to monitor negative ions, *i.e.*, a negative electric field gradient is applied to the drift tube, thermal electrons are the only background species present in the detector. Addition of oxygen to either the drift or make-up gas flows causes a reduction in the thermal electron population and production of negative reactant ions of the form $(H_2O)_nO_2^-$, where the value of n depends on the water concentration in the instrument[18]. Such results are in agreement with studies on electron-capture detectors, where oxygen doping has been shown to increase detector sensitivity to compounds with a small number of halogen atoms[19–21]. The $(H_2O)_nO_2^-$ reactant ion peak has a reduced mobility, K_0, of 2.76 cm^2 V^{-1} sec^{-1}, which may be calculated from the drift time of the peak down the electric field by means of the following equation:

$$K_0 = \frac{d}{tE} \cdot \frac{273}{T} \cdot \frac{P}{760}$$

where d = ion drift length in centimeters, t = drift time of the peak in seconds, E = electric field gradient in volts per centimeter and T and P are the experimental temperature and pressure, respectively. The detector may be tuned to monitor the

drift time corresponding to the $(H_2O)_nO_2^-$ ions, resulting in a standing current analogous to that observed in a direct current oxygen-doped electron-capture detector. Compounds capable of reacting with these ions undergo dissociative or associative electron capture to form negatively charged product ion species. A depletion in the population of $(H_2O)_nO_2^-$ ions is therefore seen as a negative chromatographic peak[18]. This operating mode may be considered nearly universal for electron-capturing compounds.

Alternately, the ion-mobility detector may be tuned to monitor selectively product ions formed in electron-capture reactions. Unlike a number of other chlorinated compounds which undergo dissociative electron capture to produce a chloride ion[18], the methyl ester of 2,4-D undergoes associative electron capture to form a quasi-molecular ion with a much longer drift time in the ion-mobility detector. At a temperature of 200°C and pressure of 700 Torr, chloride ions may be observed at a drift time of 5.94 msec ($K_0 = 2.92$ cm^2 V^{-1} sec^{-1}) whereas the 2,4-D product ion is observed at a drift time of 7.90 msec ($K_0 = 2.19$ cm^2 V^{-1} sec^{-1}). Occasionally, an electron-capturing compound will undergo both dissociative and associative electron capture, in which case two product ions are seen. Monitoring only one product ion could result in reduced detector sensitivity to the compound if neither mechanism predominated. However, this is not the case for 2,4-D, which exhibits only the aforementioned product ion. The $(H_2O)_nO_2^-$ and Cl$^-$ ion peaks slightly overlap in the ion-mobility detector, thus requiring that oxygen doping be kept at a low level if
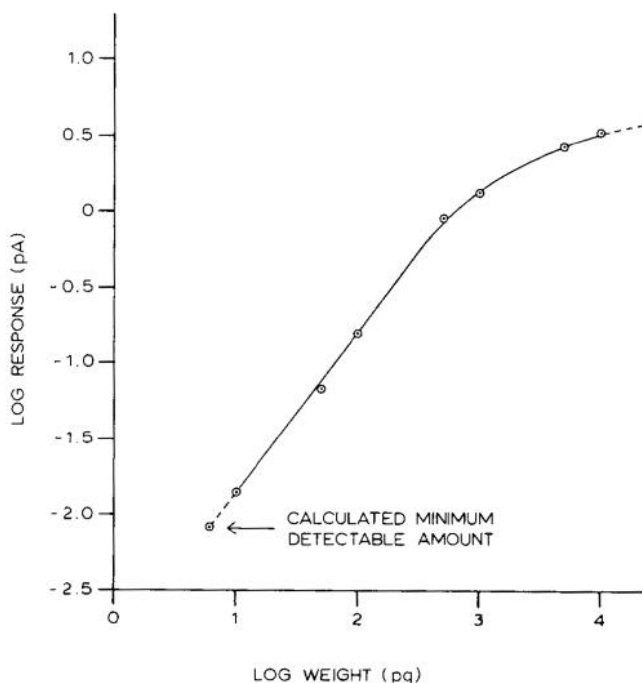

Fig. 1. Calibration graph for the methyl ester of 2,4-D, obtained by monitoring a drift time of 7.90 msec in the ion-mobility detector. Minimum detectable amount = 6 pg.
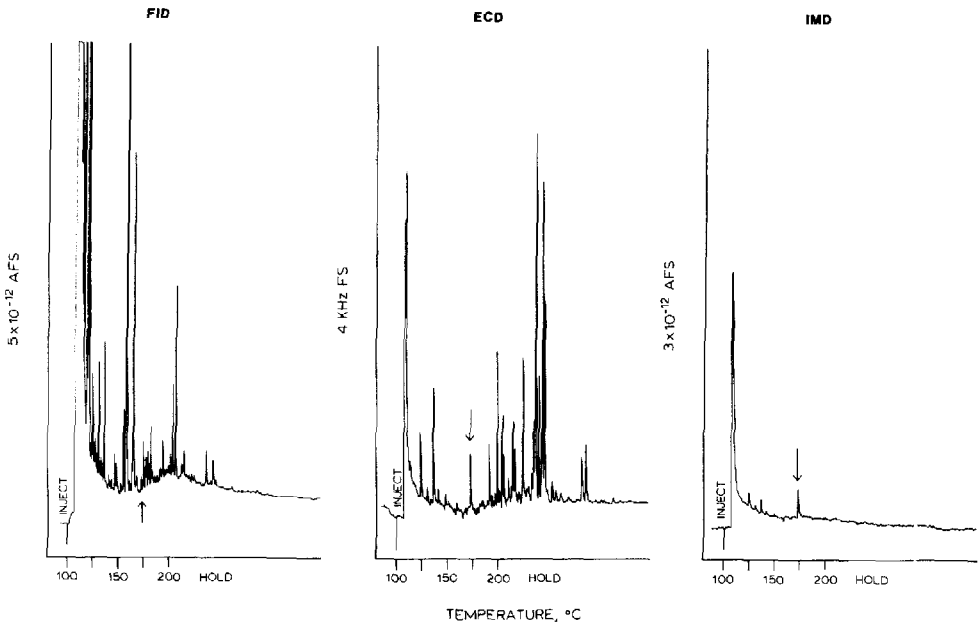
Fig. 2. Comparison of flame-ionization detector (FID), electron-capture detector (ECD) and ion-mobility detector (IMD) responses to a typical soil sample collected at Walla Walla, Washington. Arrow denotes the retention time of 2,4-D methyl ester. Concentration of 2,4-D in the original soil = 235 ppb.

chloride ions are to be observed without interference[18]. As no chloride ions are being monitored when the ion-mobility detector is tuned to detect 2,4-D, oxygen doping has been increased to improve sensitivity. Unambiguously establishing the identity of the 2,4-D product ion would require a mass spectrometer interfaced to the ion-mobility detector. Unfortunately, such an instrument is not currently available in this laboratory.

Tuning the ion-mobility detector to monitor ions with a drift time of 7.90 msec allows the selective detection of the methyl ester of 2,4-D in the presence of a wide range of other halogenated compounds. Fig. 1 illustrates a calibration graph obtained in this operating mode. The chromatographic conditions were the same as those used for analysis of soil samples. The minimum detectable amount, calculated as twice the peak-to-peak noise level of the detector, was determined to be 6 pg. The detector response is exponential with a slope of 0.92 over the linear portion of the graph. The results agree with those obtained by Tou and Boggs[22] on a commercial ion-mobility instrument. This calibration graph was used for quantification of 2,4-D residues in all soil samples studied. The concentrations listed in the figure captions represent average values obtained from carrying three portions of each sample through the entire procedure. The reproducibility was ±5%.

Although simple solvent extraction techniques are adequate to remove 2,4-D from soils[6,7], all samples used in these studies were Soxhlet extracted with acetone–hexane to remove as many organic compounds as possible. Although such an exhaustive extraction technique is not required, or even necessarily advisable, for routine 2,4-D determinations, it was desired to test the ability of the ion-mobility detector to

detect selectively 2,4-D in samples that were as complex as possible. The three chromatograms shown in Fig. 2 directly compare the performances of flame-ionization, electron-capture and ion-mobility detectors when applied to a typical soil sample. The soil was obtained from a garden in a residential area of Walla Walla, Washington. Farmers in the Walla Walla valley, a rich agricultural area in southeastern Washington with major crops, including peas, wheat and onions, often use 2,4-D to control broadleaf weeds. The chromatogram produced with the flame-ionization detector best exemplifies the complexity of the sample. The flame-ionization detector responds non-selectively to organic compounds with peaks observed for a number of species. Only a small response, as denoted by the arrow, is seen for the methyl ester of 2,4-D. The flame-ionization detector is not generally used for detection of halogenated compounds in complex samples, and quantification of 2,4-D in this instance would be extremely difficult owing to interfering peaks. The electron-capture detector is routinely used for the determination of 2,4-D residues and provides a better response. Most of the interferences observed in the chromatogram obtained using the flame-ionization detector have been significantly reduced or eliminated by the use of the more selective electron-capture detector. The ion-mobility detector, tuned to monitor the 2,4-D product ion, provides a much more selective response than the electron-capture detector to this herbicide. As discussed previously, this ion has a drift time of 7.90 msec in the drift tube. Selected-mobility monitoring has eliminated all potentially interfering components from around the peak of interest, thereby allowing unhindered quantification of 2,4-D. Relating the response back to the calibration graph yielded a value of 235 ppb of 2,4-D in the original soil.

In this soil sample the electron-capture detector could have been used to quantify 2,4-D, because interferences, observed as small peaks and minor baseline fluctuations before and after the 2,4-D response, were negligible. However, the amount of 2,4-D in this sample was relatively high, eliminating the need to concentrate the esterified soil extract appreciably prior to GC analysis. In a soil sample with a significantly lower concentration of 2,4-D, such interferences could hamper quantification with an electron-capture detector unless pre-chromatography cleanup steps were added to the procedure. With selected-mobility monitoring the ion-mobility detector would continue to discriminate against interfering compounds as the sample was concentrated. It may also be noted that the electron-capture detector appears to provide a more sensitive response than the ion-mobility detector. This is due, in part, to slightly broadened peaks observed with the latter. The last 3 ft. of the GC column are routed through a transfer line, held at 200°C, when the ion-mobility detector is in use. This would be expected to cause minor peak broadening effects in the column not seen when the entire column is temperature programmed for use with either the flame-ionization or electron-capture detector. It is planned to relocate the ion-mobility detector to the detector tray of the gas chromatograph in the near future to eliminate this effect.

The ion-mobility detector provides an additional important advantage over the electron-capture detector. With the latter, retention time is the only means of confirming that the response seen is actually due to the compound of interest. Selected-mobility monitoring with the ion-mobility detector adds further evidence, together with retention time, that the peak detected is produced by the methyl ester of 2,4-D. Ion-mobility detectors do, however, rely on the size and charge of an ion as well as its

mass to provide selectivity and therefore do not achieve absolute mass identification as do mass spectrometers. Ion mobilities should always be considered in conjunction with other information, such as retention time, in attributing a response to a specific compound. For example, several small peaks are seen prior to the 2,4-D response in the chromatogram obtained with the ion-mobility detector shown in Fig. 2. These compounds fortuitously respond in the same drift time window as 2,4-D. A response due to the methanol solvent and low-boiling products of the esterification procedure is also observed.

The two chromatograms in Fig. 3 illustrate the ability of the ion-mobility detector to detect selectively 2,4-D in the presence of a severely overlapping contaminant peak. This soil sample was obtained from agricultural land in Tennessee. In the chromatogram on the left, the detector was tuned to monitor the $(H_2O)_nO_2^-$ reactant ions present under oxygen-doping conditions. Compounds entering the detector which react with these ions produce negative responses, corresponding to a depletion in reactant ion current. This operating mode is similar to that of an oxygen-doped d.c. electron-capture detector and is non-selective for electron-capturing com-
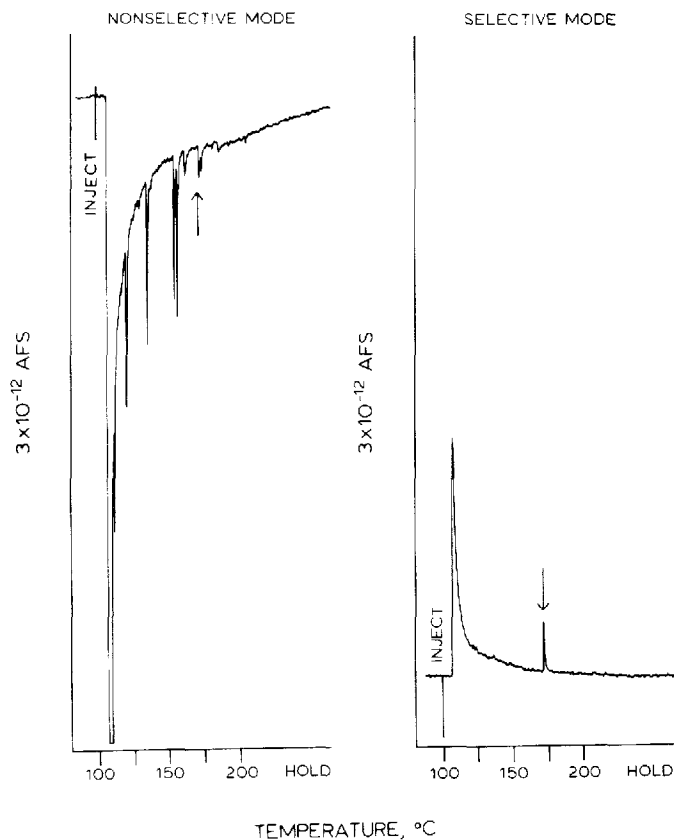

Fig. 3. Non-selective reactant ion mode and selective product ion mode chromatograms obtained on a Tennessee soil sample. The peak interfering with quantification of 2,4-D in the non-selective mode is eliminated by selectively monitoring the 2,4-D product ion. Concentration of 2,4-D in the original soil = 469 ppb.

pounds. Notice the component eluted just after 2,4-D. Total elimination of this contaminant is achieved by monitoring the drift time of the 2,4-D product ion. The chromatogram on the right in Fig. 3 was obtained by tuning the detector to monitor ions with a drift time of 7.90 msec. Only one peak, due to the methyl ester of 2,4-D, is observed. Correlation of this response with the calibration graph established a 2,4-D concentration of 469 ppb in the Tennessee soil sample.

In order to quantify reliably 2,4-D in soils, it was necessary to determine the recovery of the herbicide by the new procedure. Numerous attempts were made to secure a soil sample free from 2,4-D from lands in eastern Washington and northern Idaho. As most of this land is either forested or devoted to agriculture, it was not surprising to find at least a trace of 2,4-D present in all samples (2,4-D is also used to control undergrowth and weeds in forests). Because solvent blanks could be run through the entire procedure without the appearance of a 2,4-D response, it was known that laboratory contamination of samples was not occurring. A soil guaran-
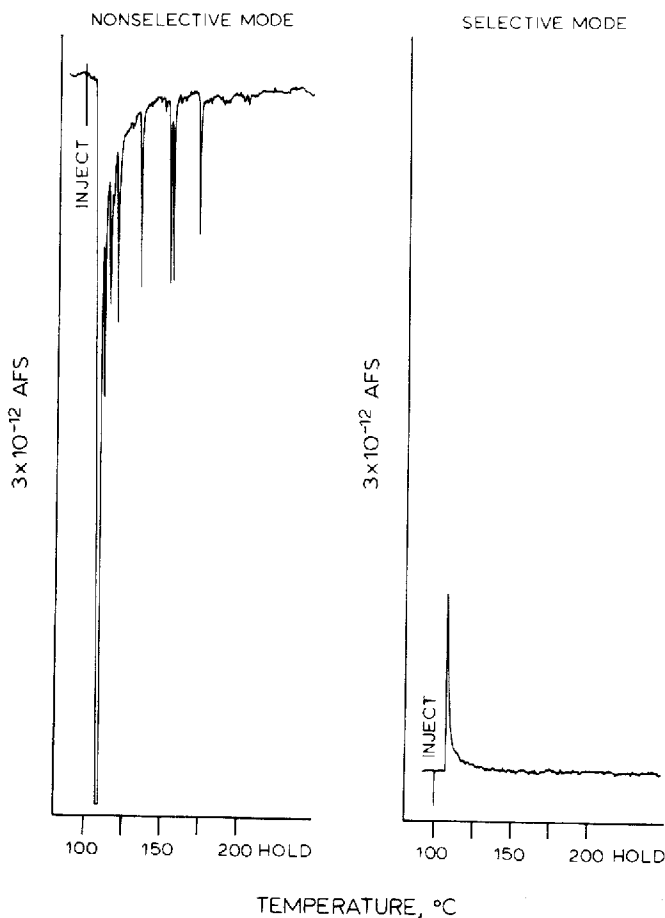

Fig. 4. Non-selective reactant ion mode and selective product ion mode chromatograms produced by analysis of a soil sample from Chehalis, Washington. No 2,4-D was observed. This soil was used for the recovery studies.

teed to be free from 2,4-D was obtained from the Washington State University Department of Agronomy and Soils. This soil, taken from Chehalis on the western side of the state of Washington, was collected and stored in 1932, before 2,4-D was available. Fig. 4 illustrates non-selective and selective chromatograms for this sample. Despite the presence of a number of electron-capturing compounds in the soil, the selective-mode chromatogram is blank. As expected, no 2,4-D was found. Spiking the Chehalis soil with known concentrations of 2,4-D at the level of 50 ppb and carrying out the full procedure resulted in an average recovery of 93%.

Because the ion-mobility detector uses a secondary ionization source, an additional study was performed to ensure accuracy in the quantification step. Response in the ion-mobility detector, as configured for these experiments, relies on the presence of $(H_2O)_n O_2^-$ reactant ions. Severe depletion of these ions by strongly electron-capturing species eluted together with the methyl ester of 2,4-D could conceivably lead to a falsely low response by the herbicide. After the response for each soil sample
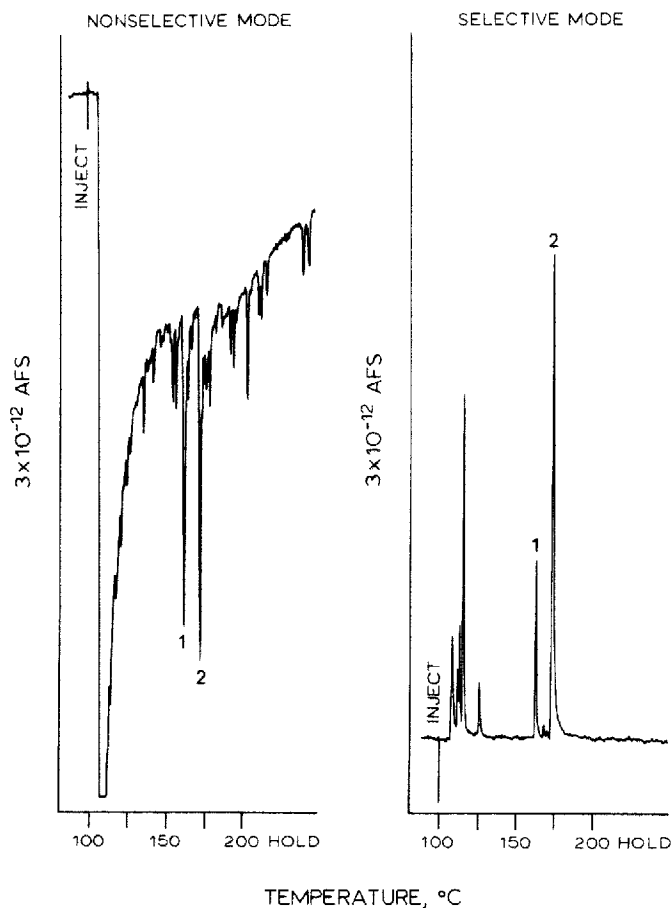

Fig. 5. Non-selective reactant ion mode and selective product ion mode chromatograms produced by analysis of a dandelion treated with Ortho Weed-B-Gon. Peaks 1 and 2 correspond to MCPP (see text) and 2,4-D methyl esters, respectively. Concentration of 2,4-D in the dandelion = 3.2 ppm.

was obtained with the ion-mobility detector, the sample was diluted by a factor of two and the new response was checked against that expected from the calibration graph. Each sample was also spiked, using a known solution of the 2,4-D ester standard in methanol, to approximately double the observed 2,4-D concentration. Predicted and actual responses were again compared. In all instances good agreement with the predicted responses was observed, indicating that reactant ion depletion was not hampering accurate quantification.

Ortho Weed-B-Gon is a popular herbicide preparation for the control of broadleaf weeds such as dandelions in lawns. Active ingredients are the dimethyl-amine salt of 2,4-D and the dimethylamine salt of 2-(2-methyl-4-chlorophenoxy)propionic acid (MCPP). Each of these herbicides is present in an amount equivalent to approximately 10% by weight of the free acid forms, the balance of the product being made up of inert ingredients. A dandelion was treated with Weed-B-Gon, extracted 48 h later and the extract was esterified by the same procedure as used for soils. Non-selective and selective chromatograms for this sample are shown in Fig. 5. Peaks 1 and 2 correspond to the methyl esters of MCPP and 2,4-D, respectively. The retention times match those obtained when a small amount of Weed-B-Gon solution was extracted, esterified and chromatographed. The non-selective chromatogram, in which the $(H_2O)_nO_2^-$ reactant ions were monitored, is complex, with a number of peaks overlapping the MCPP and 2,4-D responses. By monitoring the drift time window of the 2,4-D product ion, the chromatogram may be greatly simplified. All peaks interfering with quantification of the herbicide responses have been eliminated. MCPP and 2,4-D have similar structures and would be expected to produce product ions with similar drift times. This is, in fact, the case as both herbicides do respond in the selective chromatogram. The reason why the MCPP response appears to be diminished relative to the 2,4-D response in the selective chromatogram is that the selected mobility monitoring window has been optimized for 2,4-D. From the calibration graph, the concentration of 2,4-D originally present in the dandelion was calculated to be 3.2 ppm.

The foregoing examples show that 2,4-D may be quantified in soil extracts without the need for time-consuming sample cleanup steps by a gas chromatograph equipped with the ion-mobility detector. A large number of soil samples were examined over a 3-month period. During these investigations, the ion-mobility detector remained free from contamination, despite the fact that extremely complex samples were continually being injected into the system. Periodic recalibration with fresh standards verified that the response remained stable. For routine qualitative and quantitative analyses of 2,4-D in soil samples either of the shorter extraction procedures mentioned earlier[6,7] could replace the lengthy Soxhlet extraction used in these studies. In any case, the tunable selective capabilities of the ion-mobility detector significantly reduce the complexity of the analytical procedure.

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