

Looking for pesticides

Advances in gas chromatography equipment and software characterize chlorinated pesticides in soil

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The introduction of portable gas chromatography (GC) devices with higher range temperature controls now means that volatile as well as semi-volatile compounds can be analyzed with the same instrument. This means high molecular weight pesticides and polychlorinated biphenyls (PCBs) can now be analyzed.

Over the past decade, the main application of portable GCs has been the detection of volatile hydrocarbons. The growth in popularity of GC use has been enhanced by the flexibility, improved accuracy and lower cost afforded by on-site measurements. Until recently, portable GCs with photoionization detectors (PID) have either had no temperature control or limited ability to control temperatures up to 50°C.

While techniques such as direct injection and headspace analysis are common for volatile hydrocarbons, different techniques are required for non-volatile hydrocarbons. The most suitable technique for quantitative removal of organochlorinated pesticides from soil or water is probably solvent extraction.

The use of pesticides is an integral part of agriculture in developed countries to destroy or control weeds, fungi, insects and other pests. The widespread use of agricultural pesticides has created additional problems due to runoff and subsequent contamination of substantial quantities of surface water as well as groundwater tables.

In addition, there are numerous sites where chlorinated pesticides have been stored or used—such as areas surrounding airplane hangars where these pesticides are loaded for aerial spraying. One problem with the chlorinated pesticides is that they do not

easily break down and thus, remain in the environment for a long time.

The Spittler extraction procedure is a simple field method which appears to be applicable for a variety of pesticides in a number of different matrices, including soil and water.

It involves taking an 800 mg soil sample or a 10 milliliter (ml) water sample, adding one cubic centimeter (cc) of a 1:4 water methanol mixture and adding one ml of hexane. Shake for 30 seconds, let stand for 30 seconds (if the mixture emulsifies, then centrifuge the sample). Inject the top layer (hexane) into the GC. This method was originally developed for the analysis of PCBs. As a result, tests were performed on the extraction efficiency of DDT and some of its isomers to determine the viability. Tests were run at the one to 10 parts per million (ppm) levels since the action level for dichloro diphenyl trichloroethane (DDT) is presently two ppm. The efficiencies of extraction from soil spiked with DDT were 95-99 percent.

Samples were analyzed on site with the portable GC but grab samples collected for laboratory analysis were stored in glass jars and analyzed within a few weeks of the time of collection. All soil samples were dried prior to weighing.

Field analyses were performed using an HNU Systems model 311 GC equipped with a PID. Following the extraction, a one μ L sample of the hexane layer was injected into a capillary injector and separated on a 15 meter by 0.32 millimeter capillary column which was maintained at 180°C. The carrier flow rate was 15 ml per minute of ultra high purity nitrogen. The GC was calibrated with a DDT standard. A dichloro diphenyl dichloroethane (DDD) stan-

dard was also run to verify that no peak overlap occurred with DDT.

A quality control (QC) protocol was maintained for the analytical results obtained in the field which consisted of analysis of a standard to determine percent recovery and analyzing duplicates on sample extracts to verify analyst reproducibility. The instrument was recalibrated at the beginning of each morning and afternoon shift and at any change in condition.

Laboratory analyses for a number of field samples were performed with a GC equipped with dual electron capture detectors (ECDs) and a retention index monitoring (RIM) system. The RIM system is a tool for the automatic interpretation and identification of complex mixtures based on a unique pattern recognition algorithm for search of index peaks. Compound identification is based on two columns of different polarity.

Separations were accomplished on a pair of 0.32 mm by 25 meter (per identification) fused silica capillary columns. The oven temperature for these analyses was 150°C. Both column inlets were installed into a single column injector.

Identifications were made with Micman identification software which compares the results on both columns to a pre-established library and then lists results only when the compound is found on both columns. Identifications were based on absolute retention time.

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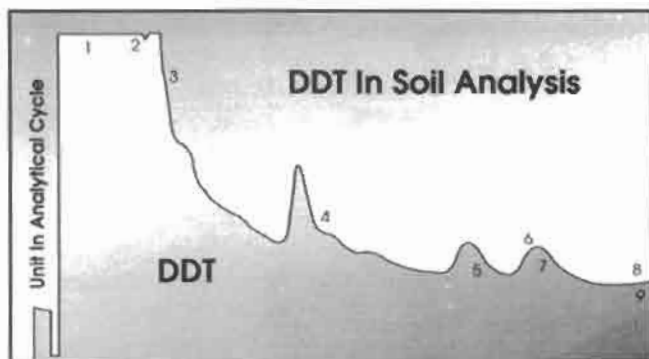


Fig. 1: Typical chromatogram of field sample measured at 10 ppm, hexane extraction.

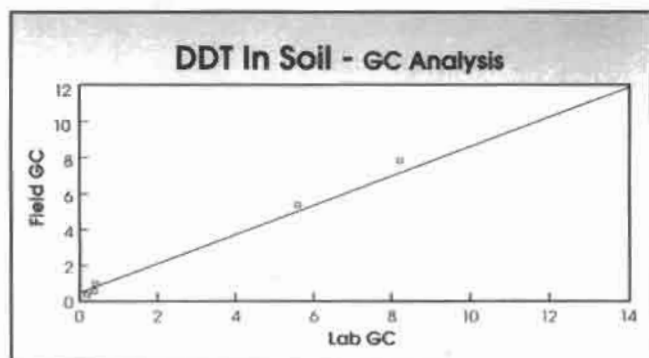


Fig 2: DDT in soil analysis—field vs. lab results shows correlation coefficient of 0.998.

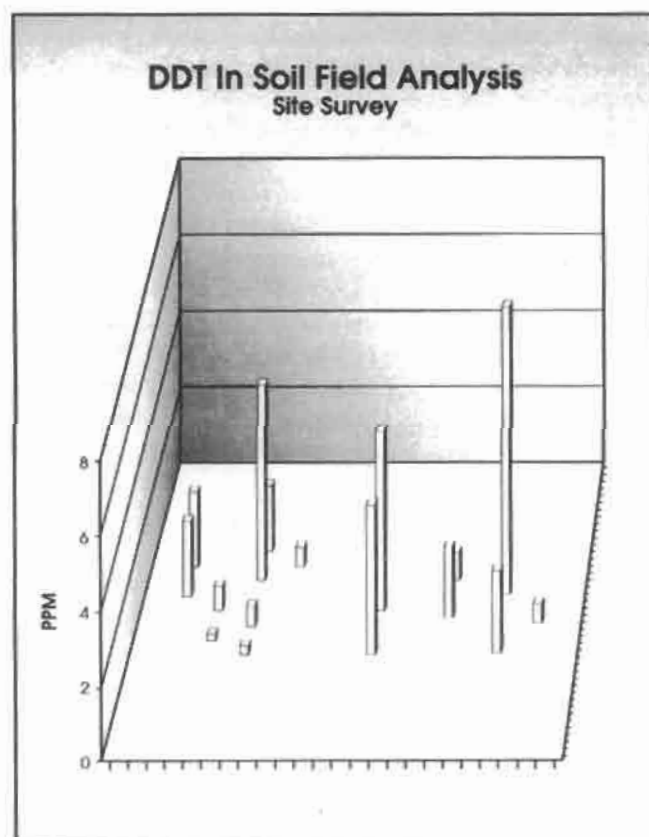


Fig 3: Three-dimensional graph of site survey visualizes spatial profile of pollutants at the site.

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Sampling was accomplished using stainless steel coring tools to depths ranging from zero to 19 inches. Surface samples were collected with stainless steel spatulas. Soils recovered from the coring device were placed in a stainless steel bowl and mixed thoroughly prior to analysis. All equipment was decontaminated between sampling depths and locations.

In the absence of any regulatory cleanup standard, the Environmental Protection Agency's (EPA's) proposed corrective action level of two ppm was used as the guideline.

The soil was manually evacuated and contained in 55-gallon steel drums. Upon completion of the first excavation lift, the bottom of the pit was sampled. Excavation proceeded to areas with concentrations of DDT at levels exceeding two ppm. This process was repeated until all concentrations in the pit were less than two ppm. The soil was disposed in a permitted hazardous waste landfill.

A typical chromatogram of a field sample measured as 10 ppm DDT is shown in Figure 1, page 13. A number of field samples were returned to the U.S. Army Corps of Engineers, Missouri River Division laboratory, for verification of

results for DDT using SW-486 method 8080.

The agreement between the field data and the laboratory results was excellent with a correlation coefficient (r^2) of 0.998 (see Figure 2, page 13). The regression equation which describes the relationship between the two variables is: $y=0.85x + 0.295$. A three-dimensional plot of the results is shown in Figure 3, above left. The X/Y axis is the plane of the hazardous waste site while the Z axis is the concentration found—expressed in ppm.

The three-dimensional image is an easy way to

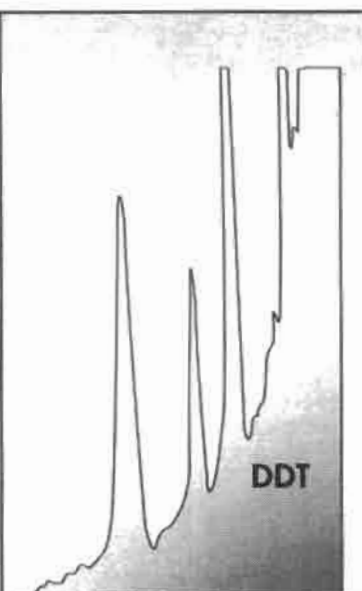


Fig. 4: Chromatogram with PID of 0.5 ppm in soil, pentane extraction.

visualize the spatial profile of pollutants at the site.

The present method of testing for DDT, which has a detection limit of about 0.2 ppm, is satisfactory for the current action level of two ppm. The method could be improved by changing the extraction solvent from hexane (IP=10.18) to pentane (IP=10.35) which has a considerably lower response to the PID. Tests have shown that DDT is still extracted with this solvent with an efficiency exceeding 95 percent. Since pentane has a lower response on the PID (10.2 eV) than hexane, it is possible to use range one, which is ten times more sensitive than range two, as required with the stronger response of hexane. The chromatogram in Figure 4, (above), in range one demonstrates the improved results obtained

with pentane. The detection limit with pentane extraction can be reduced to < 0.05 ppm.

The chromatogram in Figure 1, page 13, with the PID indicated that the major peak was DDT, although a number of minor peaks were noted.

The chromatogram in Figure 5, (right), demonstrates both the sensitivity of the ECD for organochlorinated compounds as well as the unique dual column sensitivities of the Micman software. In Figure 6 (below), other chlorinated isomers of DDT were identified along with low levels of malathion—which was not supposed to be present at this site. Note that the peaks for DDD and dichloro diphenyl ethane (DDE) elute before DDT in Figure 2, page 13, but the lower sensitivity of the PID on range two makes these peaks appear quite small. The peaks with a longer retention time than DDT do not appear to be pesticides since there was no response with the ECD. They are hydrocarbon impurities in the solvent. The detection limit for DDT with the ECD was less than one ppb (part per billion).

This particular hazardous waste site had been visited twice with samples sent for laboratory analysis. On the third visit with the on site analysis, additional areas of contamination were observed that had been undetected previously, in spite of 44 sample analyses. This type of discovery is not unusual and serves to highlight the benefits of using on site analysis equipment.

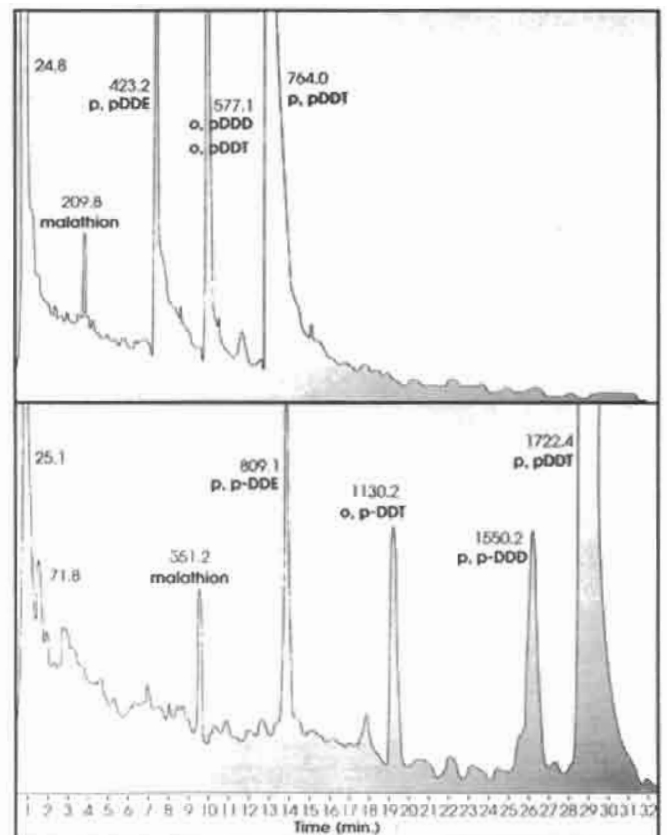


Fig 5: Chromatograph with ECD of DDT and isomers in soil.

Fig. 6: Micman System to identify pesticide compounds using absolute retention times

COMP NO. & NAME	RT. TIME	AREA	ID PARA.	DIFF.	AMT.
3 malathion	209.76	16232	209.760	7.060	.09712
	551.20	5604	551.200	-.200	.08574
12 p,p-DDE	423.20	78652	423.200	1.200	.46405
	809.12	21480	809.120	.320	.32905
14 p,p-DDD	577.12	73675	577.120	-1.28	.43468
	1550.24	22995	1550.240	-.160	.35237
15 o,p-DDT	577.12	73675	577.120	-1.28	.43479
	1130.24	11577	1130.240	-.760	.17741
16 p,p-DDT	764.00	1856068	764.000	3.200	10.95354
	1722.40	782936	1722.400	.400	11.99803
TOTAL					12.38418
					12.94260

NOTE: ALL REFERENCE STANDARDS A:0. ALL UNITS EXPRESSED IN PPM.

The combination of the Spittler extraction technique with a portable GC equipped with a PID results in good field analysis for DDT in soil. These data were in high correlation with laboratory data. The method is useful to one-quarter of the two ppm action level with hexane as the extracting solvent and to 1/40th of the action level with pentane. And, this method demonstrates that volatile and semi-volatile compounds can be run on the same GC with a PID.

The original method was described for the analysis of PCBs. Since PCBs also respond with excellent sensitivity, these species could also be determined with a GC. An obvious advantage of using the PID for analysis of PCBs is that the response does not vary with the degree of chlorination like the ECD, thus it could provide a better quantitative method for the various PCB isomers. ■