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ANALYSIS OF PESTICIDE RESIDUES BY POLAROGRAPHY

Analysis of Pesticide Residues by Polarography

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Polarography is a rapid, sensitive, and relatively specific technique that can be applied to pesticide residue analysis. The technique should also prove a valuable tool in overall pesticide research, such as monitoring new columns, studying kinetics, identifying and determining metabolites, assaying primary pesticide standards, and conducting stability studies.

Polarography is used for the detection, identification, and determination of trace components that are present in less than microgram amounts. This technique is as good as, and often better than, many of the classical methods used for the determination of a major constituent of a sample.

A number of polarographic methods for pesticide residues have been proposed. With the advent of newer, more sensitive, and more versatile polarographs on the commercial market, this technique appears even more promising for determining pesticide residues.

Basic Principles

Meites (1) defines polarography as a branch of electroanalytical chemistry that deals with the measurements and interpretation of current-voltage relationships during the electrolysis of a solution between two electrodes, one of which is very small.

The small electrode is usually a dropping-mercury electrode (DME) because it is easily polarizable and has the unique property of giving exactly reproducible results. The other electrode is nonpolarizable and is referred to as the reference electrode.

The polarized or polarizable electrode adapts the potential externally impressed on it with little or no change in the rate of electrode reaction, i.e., no change in current. The depolarized or nonpolarizable electrode retains a constant potential independent of the current and is not altered by the changes in applied potential. Therefore, if only one electrode in a cell is polarizable, its poten-

tial will change by the same amount as the change in applied potential.

Polarography consists of gradually applying an increasing potential difference between a polarizable and a nonpolarizable electrode in a solution and measuring the currents produced in microamperes. These currents are caused by the migration of ions to the DME in the electrical gradient set up around it and the diffusion of ions into a concentration gradient formed by the removal of ions from the solution immediately surrounding the electrode. This latter current is called the diffusion current and is the current of interest in polarography.

The current due to migration of ions to the DME is suppressed by adding an indifferent salt to the solution in a concentration of at least 35 times that of the oxidizable or reducible substance. This indifferent salt is called the *supporting* or *base* electrolyte and is not itself oxidized or reduced over the potential range being studied. This salt also serves to increase the electrical conductivity of the solution, and in so doing, decreases the potential or IR drop through the cell.

If a solution contains an oxidizable or reducible substance, a reaction will take place at the DME. The potential at which this reaction takes place is a function of the reduction or oxidation potential of the electroactive species and, in a given solution, is characteristic of the substance being oxidized or reduced. The diffusion current produced depends on the concentration of the oxidizable or reducible substance in the solution. A typical current-voltage curve is shown in Fig. 1.

As the potential increases from A to B, no reduction takes place at the DME and we note only a small, steady increase in current. This is known as the *residual current;* it is independent of any specific ion. At B, the reduction potential of a reducible ion in the solution is reached, and the current increases
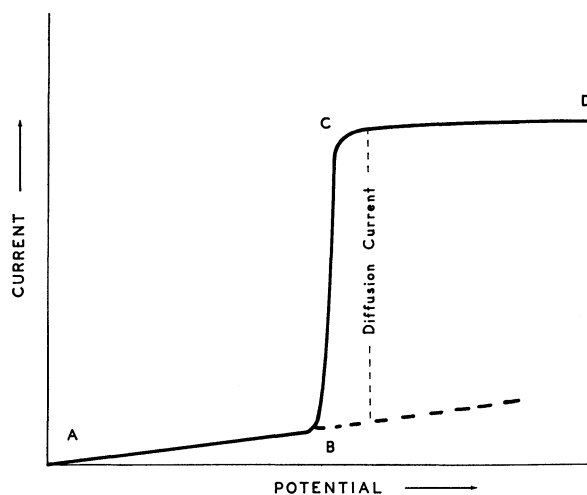
Fig. 1—Typical current voltage curves.

sharply to C. At this point the effective concentration of the reacting ion at the DME is zero, and the diffusion rate becomes constant and is proportional to the concentration of the reacting ions in the rest of the solution. A state of concentration polarization now exists at the DME and a steady current flows, as is indicated, from C to D. This current is known as the *limiting current*. The difference between the limiting current and the residual current is known as the *diffusion current*. This is proportional to the concentration of the reacting ion in the solution.

Since it is difficult to measure the reduction potential accurately, the potential at which the diffusion current reaches half the value of the limiting current is used. This is a physical constant; it is practically independent of the concentration and is characteristic of the electroactive substance. We call this potential the *half-wave potential* of the substance or E½. Since half-wave potential of a substance depends on the base electrolyte and the reference electrode used, these parameters should be specified when an E½ value is cited.

The theoretical aspects of these various polarographic currents have been studied extensively, and equations for them have been formulated by Ilkovič (2), von Stackelberg (3), and others. Detailed accounts of these investigations may be found in the

original papers of these investigators or one of the many good basic texts on polarography (1, 4, 5).

Instrumentation

A number of newer and more sophisticated polarographs are now commercially available. They are based on newer techniques, such as AC, fast sweep hanging drop, square wave, multiple and single sweep oscillographic, and pulse polarography.

We have used three types of polarographs for pesticide residue determinations in our laboratory: a conventional, recording polarograph, the Sargent XXI; a single-sweep cathode ray polarograph, the Polarotrace K1000; and a newer dual cell cathode ray polarograph, the Davis Differential Cathode-Ray Polarotrace 1660.

The conventional recording polarograph does not have the sensitivity required for residue analysis, although it is adequate for analyzing substances in the semimicro range. Therefore, we turned to the single-sweep cathode ray polarographs because of their greater sensitivity, speed, versatility, and ease of operation.

In single-sweep oscillographic polarography, the potential change is rapidly applied and is restricted to the life of a single drop. The trace observed represents the electrode reaction taking place during the

last 2 seconds of drop life of a single drop, when its growth rate is smallest. There is a 5 second delay period during which each drop is growing. Thus, we get a complete polarotrace every 7 seconds, the lifetime of each drop.

The rapid application of the voltage change gives rise to characteristic peak-shaped waves, as shown in Fig. 2. The peak is not a polarographic maximum but is due to the rapidity of the reaction at the DME. AB corresponds to the residual current, BC corresponds to the diffusion current, and CD falls off to a modified limiting current. The peak height BC is proportional to the concentration, and because of various factors, the sensitivity is greatly increased. The main factor is elimination of the drop wave, i.e., curves due to the growth and fall of successive drops. The potential at the peak is known as the *peak potential* and closely resembles the $E\frac{1}{2}$ of conventional polarography. It is usually about 0.05 v more negative. Equations for these waves have been formulated by Delahay (6) and by Randles (7).

Circuit modifications make it possible to use the instrument for derivative polarography, a measure of the rate of change of the current with voltage against voltage, di/de vs. E, instead of current vs. voltage. When the derivative circuit is used, better resolution is achieved; however, sensitivity is lost by a factor of 10.
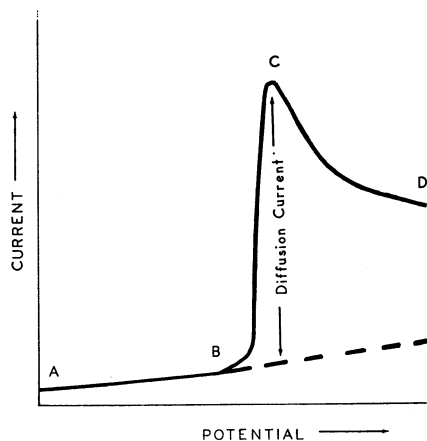
Recently, a new cathode ray polarograph described by Davis and Rooney (8) has become commercially available. This instrument, the Davis Differential Cathode-Ray Polarotrace 1660, contains many new features developed from the advances in electronics over the past decade since the K1000 was introduced. As in the K1000, a polarogram is traced once every 7 seconds. The drop time is automatically synchronized, however, so that operation is smoother and easier. The new Polarotrace is a dual cell instrument, and these cells are easily balanced. This permits four distinct modes of operation:

(1) *The subtractive mode of operation;* when one cell contains the sample solution and the second cell contains a sample or reagent blank. Any effects due to reagent impurities are canceled out so that the sensitivity of the instrument is greatly increased.

(2) *The comparative mode of operation;* used when the approximate composition of the sample is known. One cell contains the sample solution and the other cell contains an accurately known standard of similar composition. The difference in wave height is due to differences in composition. Measurement can be made with a precision of $\pm 0.1\%$. This mode of operation is most useful in the analysis of major components, i.e., primary standards, alloys, etc.

(3) *The twin cell derivative mode of operation;* in which both cells contain the same solution and a small preset difference is maintained between the applied potentials. This mode results in a derivative wave form, which permits the resolution of waves only 0.04 v apart. When a parallel resistance-capacitance network is introduced into the amplifier system, a second derivative is obtained, which results in the resolution of waves only 0.025 v apart.

(4) *Single cell instrument mode of operation;* this instrument has provisions for baseline slope compensation and current zoning controls, so that it is possible to measure a very low concentration of a substance in the presence of much higher amounts, 1000 to 1, of a more electropositive ion.
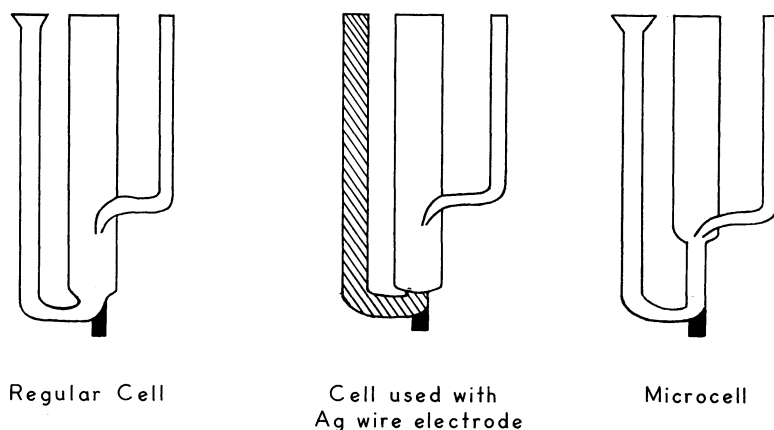
Fig. 2—A typical cathode ray polarotrace.

Regular Cell   Cell used with   Microcell
                       Ag wire electrode

Fig. 3—Cells used with Polarotraces K1000 and 1660.

The most common reference electrodes are the standard calomel, the mercury pool, and the silver wire electrodes. We generally prefer the silver wire reference electrode (#20 or #22 gauge silver wire coated with a very thin layer of AgCl) for trace analysis with the conventional and the single cell cathode ray polarographs. This electrode is suitable for microanalysis and for routine work because it does not require special cells, does not take up much room, and is easy to clean or replace. When the dual cells are used for subtractive, comparative, or differential analysis, mercury pool electrodes are preferred since they are more easily reproduced—that is, each cell will have the same reference electrode—and thus it is easier to balance them.

There are many different kinds of polarographic cells. Zagórski (9) has written a fine review on the various kinds of cells and their uses. He states: "Because all the phenomena of polarographic electrolysis occur at the surface of the mercury drop, the volume and shape of the cell containing the solution has little effect on the reaction." Polarographic analyses have been carried out in huge volumes of solution, on one hand, and in only a fraction of a milliliter, on the other.

The cells used with the cathode ray polarographs are shown in Fig. 3. For ease of operation and a saving of mercury with the silver wire electrode, we have modified the cell by sealing off the right-hand side.

We have further redesigned this type of cell for micro work, as shown in Fig. 3. With this cell, as little as 0.5 ml of electrolyte solution can be polarographed.

Clean mercury is essential for polarographic analysis. Mercury cleaned by the method of Gordon and Wichers (10) is sufficiently pure for organic analysis. Triple distillation is necessary only when the mercury has been contaminated by noble metals. A modification of Gordon and Wichers (10) method is as follows:

Transfer mercury to 1 L thick-walled filtering flask. Add 250 ml 20% (v/v) HNO_3 and bubble a strong air current through solution mixture for 4–6 hours. Transfer mixture to separatory funnel and draw off the mercury into a clean, dry 1 L filtering flask. Add 250 ml distilled H_2O and bubble air through the mixture for about 2 hours. Pour off the H_2O layer and check its pH. Continue washing the mercury with distilled H_2O in this manner until the H_2O is neutral. Transfer the mercury and H_2O to a separatory funnel and draw off the mercury through a filter paper, S & S #589 or equivalent, having a pin hole at the apex. Catch the mercury in a clean, dry beaker. Repeat the pin hole filtration twice more and collect the mercury in a clean, dry bottle with a glass stopper for storage.

Organic Polarography

Functional Groups

Any compound which contains highly polar or conjugated unsaturated groups probably can be polarographically reduced or oxidized at the dropping-mercury electrode. The polarographic reactions of these groups are influenced by the rest of their molecules. Thus, the determination of these functional groups affords a means of determining the whole molecule.

In inorganic polarography, most of the analyses are based on reversible reactions, where as in organic polarography, reactions of most of the functional groups which are polarographed are irreversible. Table 1 lists some common irreversible functional groups.

Many heterocyclic and organometallic compounds also produce irreversible waves. Reversible reactions have been attributed to the quinoidal compounds such as benzoquinone and naphthoquinone. Certain functional groups such as thiols, R-SH, and diethyl dithiocarbamates,

$$R_2-N-C\underset{S}{\overset{S}{\diagup}}$$
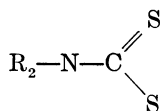
yield insoluble or complex compounds with mercury, and these compounds give anodic waves. Some nitrogen-containing heterocyclics produce catalytic hydrogen waves. In the presence of ammoniacal cobalt or nickel solutions, other compounds, such as cysteine and proteins, give catalytic waves. This type of compound usually contains at least one atom of sulfur. This is the basis of the Brdička (11) protein reaction for the detection of cancer.
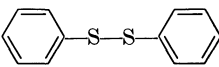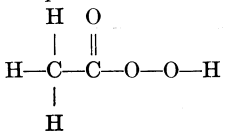
General Techniques

Zuman (12) divides organic polarographic analysis into two main categories: direct methods and indirect methods. Direct methods are those in which the samples are dissolved, the electrolyte added, and the resulting solution polarographed. Indirect methods are used for those compounds which are polarographically unreactive in themselves, but which can be transformed by a chemical reaction into reactive com-

Table 1. Common irreversible functional groups

Functional Groups	Examples
Conjugated double or triple —C=C—C=C— —C≡C—C≡C—	butadiene $\overset{H}{\underset{}{|}}\ \overset{H}{\underset{}{|}}\ \overset{H}{\underset{}{|}}\ \overset{H}{\underset{}{|}}$ C=C—C=C H H
Carbon-halogen C—X	chloroform Cl	H—C—Cl	Cl
Carbon-oxygen C=O	formaldehyde O ‖ H—C \ H
Carbon-nitrogen C=N	acetamidine H H	/ H—C—C—N	‖ \ H N H	H
Nitrogen-nitrogen —N=N—	azobenzene ◯—N=N—◯
Nitrogen-oxygen —N=O	nitrobenzene NO₂	◯
Carbon-sulfur —C—S	diphenylsulfone O ‖ ◯—S—◯ ‖ O

(Continued)

Table 1. (*Continued*)

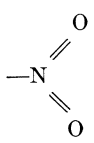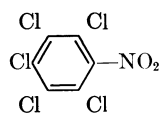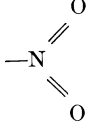| Functional Groups	Examples
Sulfur-sulfur —S—S—	diphenyl disulfide
Oxygen-oxygen —O—O—	peracetic acid
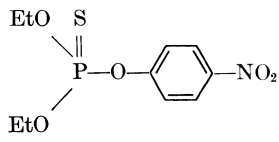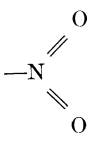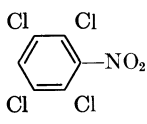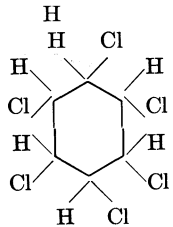
pounds. Nitration, nitrosation, condensation, addition, substitution, oxidation, hydrolysis, and complex formation are reactions commonly used in indirect methods.

Polarographic methods, like other techniques, require some type of preliminary separation. The techniques most commonly used are extraction, distillation, dialysis, electrophoresis, precipitation, complex formation, and chromatography.

Pesticide Analysis

We first study the structure of the pesticide under investigation for the presence of a polarographically reactive functional group or for reactions necessary to obtain a derivative possessing such a group. We then search the literature on polarography for the best way to polarograph these functional groups. The literature sources we have found to be most helpful are "Polarography in Medicine, Biochemistry, and Pharmacy" by Březina and Zuman (13), "Organic Polarographic Analysis" by Zuman (12), and "Progress in

Table 2. Pesticides determined by the direct method

Pesticide	Formula	Functional Group	Reference
Parathion			Ott and Gunther (19) Martens, *et al.* (20) Bowen and Edwards (21) Gajan (22) Nangnoit (23)
TCNB (Fusarex®)			Webster and Dawson (24)
PCNB (Terrachlor®)			Bache and Lisk (25) Gorbach (26) Klein and Gajan (27)
BHC		C—Cl	Cieleski and Josepovits (28) Dragt (29) Ingram and Southern (30)

(Continued)

Table 2. (*Continued*)

Pesticide	Formula	Functional Group	Reference
DDT		C—Cl	Keller, *et al.* (31) Meltzer (32) Gajan and Link (33)
Dieldrin		C—Cl	Swanepool (34)
TMTD (thiram) (—S—S— group)		—S—S	Nangnoit (35)
Guthion (>C=O group)		>C=O	Bates (36) Nangnoit (23)

Polarography" in two volumes, edited by Zuman and Kolthoff (14). Volume 2 contains excellent chapters by Elving (15) on organic analysis and by Tachi and Senda (16) on industrial analysis in which they devote a liberal section to pesticide analysis. Wawzonek (17, 18) has also reviewed organic polarography. Table 2 lists some of the pesticides that have been polarographed directly and their polarographically reactive functional groups. Table 3 lists some pesticides that have been determined by the indirect method.

To be polarographed a compound must be in solution and must remain in solution after the addition of a base or supporting electrolyte. Because of the low solubility of many of the pesticides under investigation, special solvents are required. Acetone, methanol, and ethanol are the most common solvents used in polarographing pesticides. Acetonitrile, dimethylformamide, pyridine, and dioxane may also be used.

In the selection of a solvent-electrolyte system care must be taken that no interfering substances are present, i.e., substances that interfere with the waves being analyzed by either having a similar half-wave potential or reducing at a more positive potential and that are present in an amount manyfold greater than the compound of interest. It is our experience that most of the interferences encountered in pesticide residue analysis have been traced to impurities, either in the solvent or in the electrolyte solution. Therefore, we recommend that all solvents used in polarographic procedures be purified and checked for purity frequently. This is done by polarographing a solution containing only the solvent and the electrolyte and checking for interfering waves over the potential range of interest. The electrolytes most commonly used in pesticide residue analysis are the salts of the alkali metals, potassium, sodium, and lithium, and the salts of the tetraalkyl ammonium com-

Table 3. Pesticides determined by the indirect method

Pesticide	Formula	Method	References
DDT		Nitration (tetranitro group)	Davídek and Janicek (37)
Carbaryl (Sevin®)		Nitrosation (oxime group)	Gajan, Benson, and Finocchiaro (38)
Malathion		Elimination (diethyl fumarate)	Jura (39) Ott and Gunther (19)
Demeton (Systox®)		Hydrolysis (group unknown) must contain $S{=}P{-}$ or $-P-S$	Gajan (40) Nangnoit (23)
Captan		Hydrolysis to	Nangnoit (41)

pounds. These salts must also be purified, as they too may contribute interferences to the system.

The choice of the solvent and the electrolyte are very important; they are to polarography what column packing and carrier gas are to gas-liquid chromatography. The half-wave potential and the ease of oxidation or reduction at the DME are directly dependent on them. For example, in a mixture containing compounds A and B, A may polarograph before B in one system, and

B before A in another. Many interferences may also be eliminated by the proper choice of the electrolyte system.

Often when the polarographic behavior of a compound or one with similar composition is reported in the literature, only minor changes, if any, are necessary in adapting these methods for residue determination. Conversely, because of the difference in electronics, etc., many of the methods described in the literature based on the conventional type of polarographs are not suitable for a

cathode ray polarograph unless some modifications are made. A systematic approach is necessary if the polarographic behavior of the compound is unknown.

The plan we use is as follows: Prepare standard solutions containing 50 and 100 μg/ml of the pesticide in question in various solvents. (Prepare daily; very dilute solutions of many of the pesticides may decompose rapidly.) Next, prepare several typical electrolyte solutions such as $0.1N$ solutions of HCl, NaOH, NaCl, LiCl, NH$_4$Cl, NH$_4$OH, NaOAC, (CH$_3$)$_4$NBr, and mixtures of these solutions. We also use the various buffer systems such as those of McIlvaine and Britton-Robinson. Then, add various ratios of sample solution and electrolyte solution to a polarographic cell and polarograph the mixture over the entire potential range of the electrolyte used to find a usable wave.

After the best solvent-electrolyte system is established, study the effects of pH, temperature, and concentration of the pesticide on the polarographic properties of the pesticide being studied. Check the minimum and maximum amounts of pesticide which can be polarographed, since this varies from compound to compound. (The peak or half-wave potential of many compounds shifts with concentration. However, in the range of concentration encountered in residue analysis this phenomenon is rarely, if ever, observed.)

Next, determine the type and amount of cleanup necessary for pesticide residue analysis. (In some instances, a pesticide residue can be polarographed after solvent extraction without further cleanup, in which case

Table 4. Sensitivity of polarographic residue analysis

Pesticide	Pure Electrolyte Solution, μg/ml	Actual Crop Analysis, ppm
Parathion	0.004	0.04
Carbaryl (Sevin®)	0.020	0.20[a]
Guthion	0.025	0.04
Malathion	0.200	0.30
DDT	0.500	0.50

[a] 10 g crop sample; all others, 25 g crop sample.

we may observe a slight shift in peak potential due to the viscosity, etc. of the uncleaned solution in the polarographic cells.)

The extraction and cleanup procedures used for other residue techniques are usually sufficient for polarographic analysis. Again, all the reagents used, especially the solvents, should be purified and checked. Occasionally interferences originating in the column packing or drying agents were found. If thin layer chromatography is used in conjunction with polarography, the adsorbents used on TLC plates should be checked carefully.

In polarographic analysis the wave height observed from the sample solution is compared to that obtained from polarographing a standard solution at the same time and under the same conditions. This is known as the comparative method. Another technique is to add a known amount of a standard to the cell solution and note any increase in wave height. From this increase in wave height the amount of pesticide in the sample can be calculated after correcting for volume change. This technique also is a valuable check on the qualitative determination, since the half-wave potential of the standard added and the compound in the sample should match if they are the same compound.

Polarography, like other instrumental methods, is a comparative technique and therefore requires a standard reference material. This standard pesticide must be a well-defined compound whose chemical composition and purity is known and adequately verified by the several techniques available.

Table 4 lists the sensitivity of some of the pesticide residue methods we have developed according to the procedure outlined above.

Future Possibilities

One of the most promising applications of polarography in pesticide residue analysis is combination with chromatography: gas-liquid, thin layer, paper, liquid-solid, and/or liquid-liquid. Kemula (42) and co-workers have developed a technique they call *chromato-polarography*, in which they join a chromatographic column to a polarographic cell and measure the volume of effluent in

a graduated cylinder. The current flowing through the cell is plotted against the volume of effluent. They called the resulting graph a *chromato-polarogram*. Kemula and Kyrzemińska (43) separated *p,p'*-DDT from *o,p*-DDT by using a column consisting of swollen rubber saturated with heptane and eluting with an electrolyte solution composed of 0.05N tetramethylammonium bromide in 85% dimethylformamide. It is interesting to note that *p,p'*-DDT eluted from this column before *o,p*-DDT. This is exactly the opposite of their elution pattern on a GLC column packed with 10% DC-200. The shape of the respective peaks is similar, as is the ratio of their respective peak heights. Sandi (44) used a similar technique to separate and determine six analogs of parathion. This chromato-polarographic technique should prove useful in evaluating and studying various columns used for cleanup of pesticide residue samples.

On several occasions we have successfully combined paper chromatography and polarography for the identification and determination of pesticide residues (40). Kováč (45) recently combined thin layer chromatography and polarography to determine the organophosphorus pesticide, Sumithion. This combination shows great promise; TLC can be used for rapid separation and identification, and polarography for verification of identity and quantitative determination.

It should also be possible to utilize the technique developed by Giuffrida (46), whereby pesticides eluted from a GLC column are trapped for subsequent IR analysis. After trapping, these eluents might just as readily be determined polarographically.

Recently Nangnoit (23) published a paper listing the results of a study of the polarographic characteristics of 24 organophosphorus pesticides in 3 different electrolyte systems. This reference should be useful to anyone who wishes to apply polarography to determine pesticide residue.

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