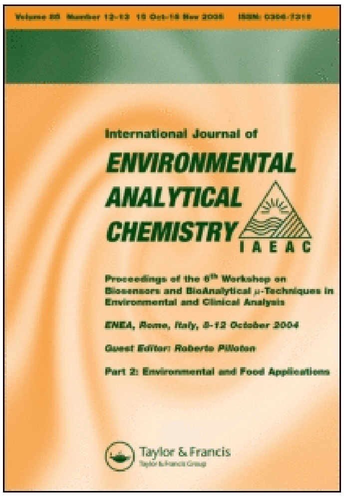

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Bourque, C. L. , Duguay, M. M. and Gautreau, Z. M.(1989) 'The Determination of Reducible Pesticides by Adsorptive Stripping Voltammetry', International Journal of Environmental Analytical Chemistry, 37: 3, 187 — 197
To link to this Article: DOI: 10.1080/03067318908026897
URL: http://dx.doi.org/10.1080/03067318908026897

Intern. J. Environ. Anal. Chem., Vol. 37, pp. 187–197
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THE DETERMINATION OF REDUCIBLE PESTICIDES BY ADSORPTIVE STRIPPING VOLTAMMETRY

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(Received 5 December 1988; in final form 14 April 1989)

The electrochemical determination of six pesticides by adsorptive stripping voltammetry is described. These pesticides are the following: the nitrated organophosphates Methyl Parathion, Parathion, Dicapthon and Fenitrothion, the asymmetrical triazine Guthion and the *s*-triazine Simetryne. Analytical response as a function of variables such as accumulation potential, accumulation time and pH is presented. The technique is shown to be 20–50 times more sensitive than analysis by DPP without prior accumulation. Relative standard deviations at the 10^{-7} M level are less than 3%. Due to sufficient electrochemical resolution, the technique can be applied to the analysis of three pesticides in the same solution. Results are reported for a variety of environmental samples. High concentrations of either electrolyte or co-adsorbants are shown to interfere. Detection limits are presented.

KEY WORDS: Adsorptive stripping voltammetry, organophosphorus pesticides, triazine pesticides, cathodic stripping voltammetry.

INTRODUCTION

Pesticides continue to be used in great quantities and in ever increasing variety, with new products being introduced each year. While the benefits of such usage are undeniable, concerns with respect to their effects on the environment remain. Continuous monitoring of these pesticides and of their metabolites in a wide variety of matrices and at extremely low concentrations represents a major objective of most environmental agencies.

The analysis of pesticides is most often accomplished using chromatographic methods.[1,2] Although offering great selectivity through column separation, the chromatographic detectors most often used do not always demonstrate the sensitivity needed and therefore preconcentration of the pesticides (usually by L–L extraction) is often required.[3] Another approach is the analysis of these pesticides by electrochemical means.[4–6] By coupling HPLC separations with EC detection, pesticides have successfully been analyzed both in the oxidative[7,8] and in the reductive[9] modes. Where selectivity requirements are not as stringent, a new EC method, adsorptive stripping voltammetry (AdSV), is capable of great sensitivity in the analysis of hydrophobic organic compounds.[10,11] This method has mostly been used in the analysis of pharmaceuticals and of metal ions present as large organic complexes. Surprisingly, the technique has not been widely used in the analysis of pesticides. Benadikova and Kalvoda[12] reported the use of AdSV in the analysis of Dinobutone, DNOK, Ametryne and Prometryne. A second report described the use of the technique in the analysis of dithiodialkylphosphoric acid pesticides.[13] The determination followed hydrolysis of the pesticides to dithiodialkylphosphates. Recently, a third use was reported by Procopio *et al.*[14] in which the fungicide Thiram was determined by cathodic stripping voltammetry in both water and soil samples. They reported detection limits of 1.2×10^{-9} M and 1.2×10^{-10} M for accumulation times of 120 and 600 seconds, respectively. These three papers would appear to be the only results reported to date describing the analysis of pesticides by AdSV. This paper describes the use of this new EC approach in the analysis of four nitrated organophosphorus pesticides and two triazine pesticides. The effects of analytical variables are presented and the technique is applied to the analysis of environmental samples.

EXPERIMENTAL

Apparatus and reagents

All voltammograms were obtained using a PAR 264A Polarographic Analyzer, a PAR 303A Static Mercury Drop Electrode and a PAR 305 Stirrer. The 303A incorporates a Ag/AgCl reference electrode and thus all potentials cited herein are with reference to this electrode. Purging was carried out using ultra-high purity N_2. All pesticides studied were obtained from Agriculture Canada (Ottawa, Ont., Canada). Stock solutions were made up by dissolving weighed amounts of the pesticide in AnalaR ethanol and were kept refrigerated. Standard aqueous solutions were prepared daily by simple dilution of stock solutions. A stock Britton–Robinson (BR) buffer solution was made up by using a mixture of boric acid, orthophosphoric acid and glacial acetic acid, all 0.04 M, and by adjusting the pH with 0.2 M NaOH to the required value. All laboratory solutions were made up using high purity water obtained from a Milli-Q Water System (Millipore). When filtering environmental samples, 0.45 μm membrane filters (Kontes) were used. All other compounds used were of analytical grade.

Procedure

A screening procedure was carried out on approximately 20 pesticides to determine whether or not the compound exhibited surface active properties. The procedure was as follows. The solution containing 1 μM pesticide and 10^{-2} M buffer/electrolyte at pH 4.5 was purged for 8 minutes with oxygen-free nitrogen. Having chosen an initial potential *E*, a voltammogram was carried out using DPP (differential pulse polarography) on a single Hg drop. The scan commenced immediately after the drop formation at a scan rate of 10 mV/sec. A new drop was formed and a second voltamperogram carried out but this time preceded by

Table 1 Optimum accumulation potential $E_{acc\,opt}$ and stripping potential E_s for the six pesticides at pH 4.5

	F	*MP*	*P*	*D*	*S*	*G*
$E_{acc\,opt}$	−200	−200	−150	−150	−600	−300
E_s	−320	−290	−280	−250	−1050	−635

F = Fenitrothion (Phosphorothioic acid 0,0-dimethyl 0-(3-methyl-4-nitrophenyl) ester).

MP = Methyl Parathion (Phosphorothioic acid 0,0-dimethyl 0-(4-nitrophenyl) ester).

P = Parathion (Phosphorothioic acid 0,0-diethyl 0-(4-nitrophenyl) ester).

D = Dicapthon (Phosphorothioic acid 0-(2-chloro-4-nitrophenyl) 0,0-dimethyl ester).

S = Simetryne (N,N'-diethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine).

G = Guthion (Phosphorodithioic acid 0,0-dimethyl S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] ester).

applying the initial potential *E* with stirring for 60 seconds followed by a 15 second equilibration period without stirring. This procedure was repeated at 100 mV intervals. If the second voltamperogram yielded a response greater than that in the first, this was interpreted as an indication of accumulation of the pesticide at the surface of the Hg drop. The above procedure could also be carried out using cyclic voltammetry. Unless stated otherwise, the voltametric parameters were as follows: mode = DPP, scan rate = 10 mV/sec, $t_{acc} = 60$ sec, pulse amplitude = 100 mV, drop time = 0.2 sec, purge time = 8 min, drop size = medium (0.16 cm^2 surface area) and stirrer = slow (400 rpm). After usage, cells were washed with 3 M HNO_3 and high purity water.

Environmental surface water samples were collected in 2L polyethylene flasks, refrigerated (4 °C) and analyzed within 7 days. Solutions were allowed to attain room temperature before being analyzed. Calibration curves were carried out on either unfiltered or filtered (0.45 μm) samples. No measurable amounts of any of the pesticides were found in any of the environmental samples investigated.

RESULTS AND DISCUSSION

Among the approximately twenty pesticides screened by the testing procedure, six were found to exhibit both adsorptive properties and reductive electrochemistry in the available potential range (i.e. +0.2 V to −1.2 V). These six can be classified into 3 groups according to their structure and electrochemical properties: (1) nitrated organophosphates—Dicapthon, Fenitrothion, Methyl Parathion, Parathion and (2) the *s*-triazine Simetryne and (3) the asymmetric triazine Guthion. As can be seen in Table 1, the nitrated organophosphates gave similar stripping potentials but different from either of the triazines. This similarity in the behavior of the nitrated organophosphates was observed in all studies undertaken. Therefore, for the sake of brevity, further results presented herein will include only those from one representative member of the nitrated organophosphates—Fenitrothion.

The effect of accumulation potential on relative response (i.e. current values normalized with maximum sensitivity = 1.0) can be seen in Figure 1. Whereas Fenitrothion is greatly affected by variations in E_{acc}, the triazines and Simetryne in particular are much less so, having a relatively wide range of optimum accumu-

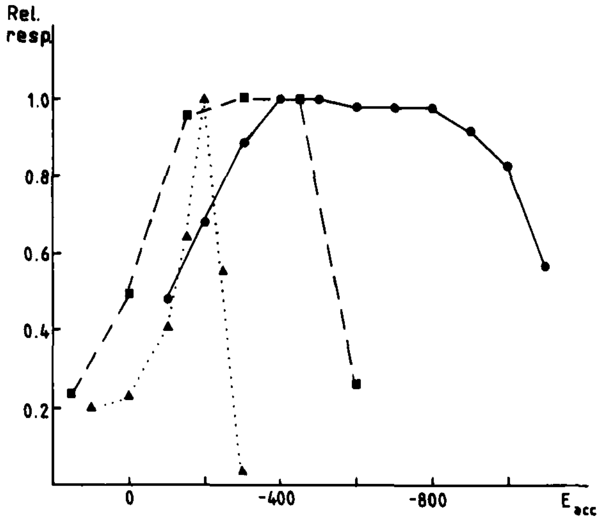

Figure 1 Relative response vs accumulation potential (mV) at pH 4.5 (acetate buffer, 10^{-2} M). ■ Guthion; ▲ Fenitrothion; ● Simetryne.

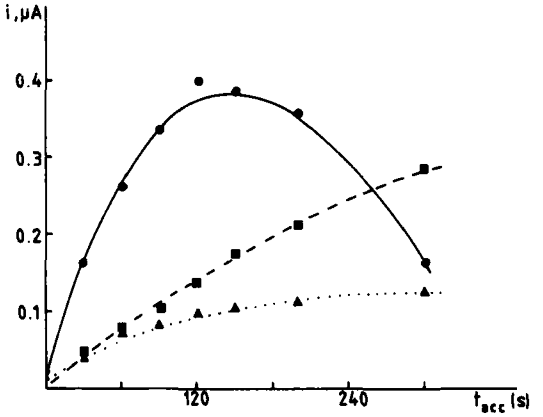

Figure 2 Current response vs accumulation time for concentrations 5×10^{-8} M. ■ Guthion, pH 5.5, $E_{acc} = -500$ mV; ▲ Fenitrothion, pH 5.5, $E_{acc} = -250$ mV; ● Simetryne, pH 5.0, $E_{acc} = -800$ mV.

lation potentials. It is therefore critical, if maximum sensitivity is to be achieved, that accumulation of group 1 pesticides be carried out at the correct potential. It was also noted that pH could influence the optimum E_{acc}. Therefore, when undertaking the study of any analyte by AdSV it is important to establish appropriate accumulation parameters for the solution matrix under consideration.

It has been shown by several authors[10,11,15] that in AdSV the current measured increases with accumulation times. This relationship is linear at short accumulation periods followed by negative curvature and eventually a levelling off as the surface of the Hg drop becomes saturated, as in a typical adsorption isotherm. Studies of response as a function of accumulation times for our 3 pesticides gave results shown in Figure 2. It can be seen that both Fenitrothion and Guthion demonstrated expected behavior at the concentration levels used (5×10^{-8} M). On the other hand Simetryne behaved quite differently, attaining a maximum after 120 seconds and decreasing significantly thereafter. This decrease in response with longer t_{acc} was found to be even more drastic at higher Simetryne concentrations (i.e. 5×10^{-7} M) and was also observed for Guthion, albeit to a lesser extent, at these relatively high concentrations. This decrease was found to be reproducible and was also influenced by pH. For example, a decrease to 22% maximum response was noted at pH 5.00 whereas the decrease was only to 51% at pH 2.95. In analyzing a standard Simetryne solution over a period of several hours, no decrease in response was noted, thereby eliminating the possibility of degradation of the pesticide in aqueous solution as the cause for the observed behavior. A more probable cause for this decrease is a degradation of the pesticide at the surface of the electrode. This degradation would appear to be both pH and concentration dependent. In accordance with results of Figure 2, t_{acc} of 120 seconds should be used in studies where sensitivity is to be optimized.

The solution pH was found to affect both the stripping potential (E_s) and the relative response at $E_{acc.opt.}$, as can be seen in Figure 3. Studies such as those in Figure 1 were carried out on solutions buffered at pH values between 2–11. By choosing the optimum accumulation potential $E_{acc.opt.}$ (i.e. where response is greatest) for each pH value and plotting this response as a function of pH, results shown in Figure 3a were obtained. Both Fenitrothion and Guthion displayed maximum response at pH 6–9 and did not show values less than 50% in the pH range studied. Simetryne, however, was found to be more susceptible to pH effects. At pH 3.0, response was greatest although the reduction peak was on the steepest part of the electrolyte wave. At higher pH, response decreased rapidly and the peak vanished completely at pH 6.0. Similar results were reported for *s*-triazines measured by DPP without prior accumulation.[16] As a compromise, optimum pH for Simetryne analysis should be at or near pH 4.0. Figure 3b indicates the effect of pH on the stripping potential. It can be seen that the relationships are linear, with slopes of 58, 57 and 62 mV/pH for Simetryne, Guthion and Fenitrothion, respectively. Published results for *s*-triazines by DPP without accumulation also gave linear relationships.[16,17] On the other hand, similar studies on Fenitrothion[18] and Methyl Parathion[19] gave curves with three and four linear segments, respectively. In both cases the reactions became independent of pH above pH 9–10. This dissimilarity in behavior suggests that the adsorption process is influencing the electrochemical reactions taking place at the electrode surface. In any case, irrespective of the processes involved, the pH appears to affect the stripping potential of the three pesticide groups similarly, resulting in a cathodic shift of approximately 60 mV per unit of pH.

The effect of ionic strength was verified by adding increasing amounts of either $NaNO_3$ or NaCl to buffered pesticide solutions and measuring the response using the optimized parameters for each. Both $NaNO_3$ and NaCl gave similar results. The accumulation of Simetryne and Fenitrothion was found to be much more susceptible to ionic strength effects than was the case for Guthion. With the former two, decreases in response were noted above 10^{-2} M electrolyte concentration, response was only 25% of maximum at 10^{-1} M and was negligible at 1 M.

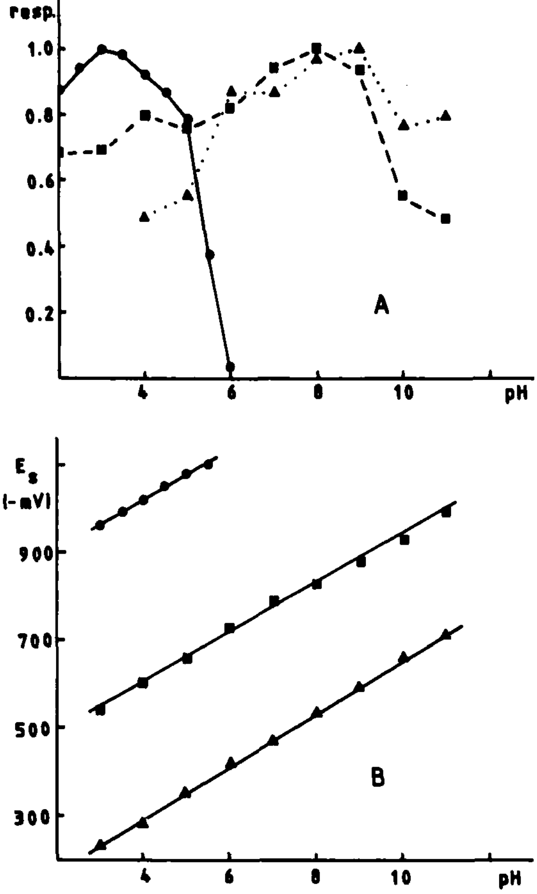

Figure 3 A—Relative response at $E_{\mathrm{acc\,opt.}}$ vs pH; B—Stripping potential E_s vs pH; Medium: 0.04 M Britton-Robinson buffer. ■ Guthion; ▲ Fenitrothion; ● Simetryne.

Guthion behaved differently, showing little or no ionic strength effects up to 1 M concentrations. It will be shown later that Guthion appears to be more strongly adsorbed than the other two pesticides and that sulfur plays an important role in this adsorption. Consequently, it is possible that the presence of two sulfur atoms in Guthion is responsible for this increased resistance to ionic strength effects. In any case only Guthion may be measured by AdSV in seawater whereas all three groups may be measured in lake or river water having low electrolyte concentrations.

Calibration curves using 60 second accumulation times for the three pesticides (buffered to pH 5.0–5.5) are given in Figure 4. Results for Simetryne indicated a linear range between 4.0×10^{-9} M and 1.9×10^{-7} M having a linear correlation coefficient (LCC) of 99.4%. Detection limits, defined as a signal-to-noise ratio of 3, gave values of 2×10^{-9} M. In comparison, DPP measurements without prior accumulation gave detection limits of 1×10^{-7} M. Guthion demonstrated linearity

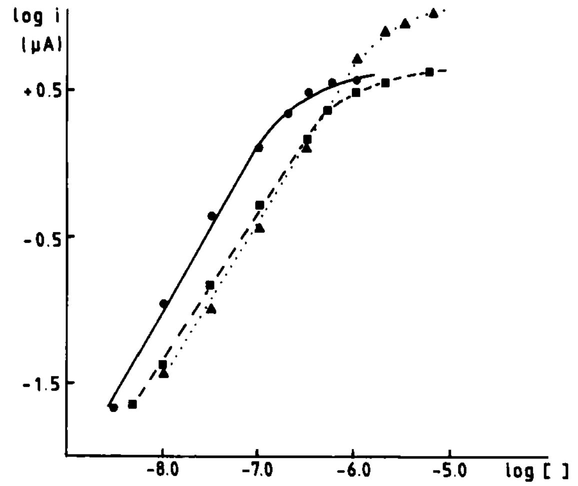

Figure 4 Calibration curves by AdSV. ■ Guthion, pH 5.0, $E_{acc} = -500$ mV, $t_{acc} = 60$ s. large drop; ▲ Fenitrothion, pH 5.5, $E_{acc} = -250$ mV, $t_{acc} = 60$ s, large drop; ● Simetryne, pH 5.0, $E_{acc} = -800$ mV, $t_{acc} = 60$ s, large drop.

over the 4.8×10^{-9}–4.8×10^{-7} M range with LCC = 99.5%. Detection limits were 2×10^{-9} M by AdSV and 1×10^{-7} M by DPP. Fenitrothion (and the other nitrated organophosphates) were found to be less sensitive. The response was linear over the 1.0×10^{-8}–6.2×10^{-6} M range (LCC = 99.6%) with detection limits of 1×10^{-8} M by AdSV and 2×10^{-7} M by DPP. Reproducibility studies (6×) at the 1×10^{-7} M levels gave relative standard deviations of 0.8%, 1.4% and 2.2% for Simetryne, Guthion and Fenitrothion, respectively. All three pesticides demonstrated a linear range of approximately two orders of magnitude, followed by curvature and levelling off, presumably as the surface of the electrode becomes saturated with analyte molecules. Slightly better detection limits can be expected by using optimum solution pH as per Figure 3a or longer accumulation times as per Figure 2. The fact that Fenitrothion is less sensitive and demonstrates less of a gain in sensitivity with respect to DPP tends to suggest that Fenitrothion is less effectively accumulated than the two other pesticides.

The large separation in stripping potentials observed in Table 1 and in Figure 3b and the accumulation characteristics outlined in Figure 1 indicate that in principle it should be possible to analyze all three pesticides in the same solution. Two approaches might be considered. One could choose a compromise accumulation potential and by scanning cathodically determine all three pesticides simultaneously. A second approach would be to determine each pesticide separately by accumulating at or near the $E_{acc.opt.}$ for each followed by a scan to determine that pesticide only. This second approach should offer the advantage of greater sensitivity but is more tedious. The second approach was carried out on a solution containing 5.0×10^{-8} M of each of the three pesticides. Determinations were done by standard additions and least squares analysis. Linearity at low concentrations was observed in all 3 cases (LCC > 99%). Results for this multipesticide determination were as follows: 4.1×10^{-8} M Fenitrothion, 5.5×10^{-8} M

Table 2 Competition studies between pesticides[a]

	Relative response[b] (%)		
0.6 μM added	*F*	*S*	*G*
F	—	77.2	71.3
S	113.6	—	69.4
G	38.8	40.5	—

[a] The effect of adding 0.6 μM of *one competitive pesticide only* on the response obtained for 0.1 μM of the pesticide being analyzed.

[b] Response in absence of added pesticide = 100 %.

Guthion and 4.5×10^{-8} M Simetryne. These multi-pesticide accumulations correspond to a competition amongst adsorbants for surface sites. Comparative studies done by adding 0.6 μM of pesticide A to a fixed amount of pesticide B and monitoring the response for B were carried out to obtain information on the relative binding strengths of the three pesticides (Table 2). It was found that Guthion was preferentially adsorbed with respect to the other 2 pesticides. No distinction could be made between Fenitrothion and Simetryne.

The preceding studies were done on samples made up by spiking distilled water with buffer and the appropriate pesticide(s). For the method to be of analytical significance, its usage must be applicable to environmental samples. Seawater samples were ruled out because of the susceptibility of Fenitrothion and Simetryne to ionic strength effects. Four sampling areas were used: (1) Petitcodiac River—a freshwater tidal river containing large amounts of resuspended sediment, (2) Turtle Creek—a small freshwater brook, (3) Turtle Creek Reservoir—an artificial lake created for municipal water supply demands and (4) a residential wellwater supply.

To find out if these environmental samples were amenable to analysis, calibration curves were obtained by incremental additions of known amounts of Guthion to either unfiltered or filtered solutions. One of the four sampling areas (Petitcodiac River) could not be effectively analyzed for Guthion because of an important decrease in sensitivity. In addition, two large peaks were observed between −150 mV and −400 mV. However, upon passing this sample through a clean-up column of either XAD-4 or Florisil prior to spiking with Guthion, these large peaks were greatly reduced and sensitivity returned to near normal levels. Similarly, if a distilled water sample was analyzed after the addition of buffer and humic acids (2 ppm), two peaks between −150 mV and −400 mV appeared having profiles similar to those observed in the Petitcodiac River sample. Quentel *et al.*[15] reported the use of AdSV in the analysis of humic substances in seawater. They used an $E_{acc} = -150$ mV and reported two peaks with similar profiles (−260 mV and −520 mV). It would thus appear that our sample contained appreciable amounts of humic matter capable of decreasing sensitivity significantly through competition for available adsorption sites. Work is now being carried out to find a rapid method of either extracting these pesticides from difficult matrices or removing the humic acids from the sample solution prior to analysis. Results for the other samples are given in Figure 5.

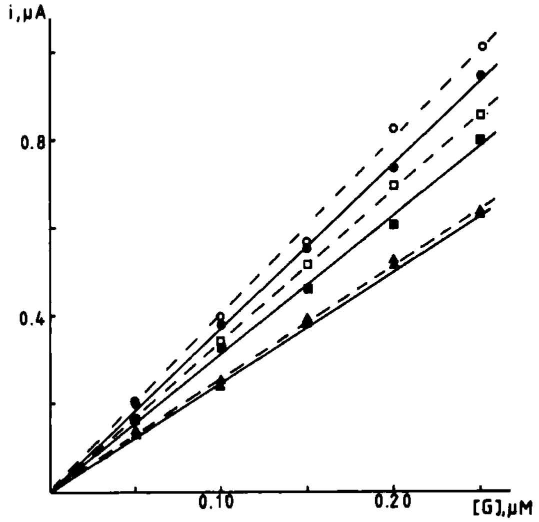

Figure 5 Guthion calibration curves in three environmental samples. Acetate buffer, 10^{-2} M, pH 5.0. $E_{acc} = -500$ mV. ■ Turtle Creek, unfiltered; ▲ Turtle Creek Reservoir, unfiltered; ● Wellwater, unfiltered; □ Turtle Creek, filtered; △ Turtle Creek Reservoir, filtered; ○ Wellwater, filtered.

It can be seen from results in Figure 5 that the three sampling areas gave linear calibration curves (i.e. LCC>99.3) for both filtered and unfiltered solutions. However, the slopes for the unfiltered samples were slightly lower than those for their filtered counterparts. These decreases in sensitivity were calculated to be 2.8%, 7.4% and 6.4% for the Turtle Creek Reservoir, the Turtle Creek and the wellwater samples, respectively. There are two possible explanations for these observed decreases in sensitivity: (1) the presence of competing co-adsorbants, (2) adsorption of Guthion onto organic or inorganic colloids (e.g. humic and fulvic acids). It would appear that the "competing co-adsorbant effect" is to decrease proportionally the response obtained by AdSV. For example, calibration curves for Guthion in the presence and in the absence of a known competing co-adsorbant pesticide (i.e. Simetryne) were linear with the former having a lower slope than the latter (similar to that observed in Figure 5). If this is true, the presence of co-adsorbants will influence sensitivity but not alter the result of the determination as measured by the standard addition technique. On the other hand, colloids capable of adsorbing pesticides may yield results lower than actual total concentrations. This is due to the fact that AdSV, in principle, only measures species in true solution and does not measure adsorbed analytes. Therefore, pesticide-adsorbing colloids should be regarded as potential interferences in the determination of "total" pesticide concentrations. However, by analyzing filtered environmental samples by standard addition, information on the speciation of the analyte is obtained. A potential use of AdSV as applied to pesticide analysis would be to measure "free" (i.e. not adsorbed) pesticide concentrations and relate results to toxicity data, as is currrently done in heavy metal ion speciation studies.[20]

To compare the method described herein with an established gas chromatographic method,[3] the wellwater sample was spiked with Fenitrothion such that its concentration was 7.5×10^{-8} M. The GC method required a L-L extraction into methylene chloride prior to analysis. Analysis by AdSV yielded 9.8×10^{-8} M whereas that by L-L extraction/GC gave 6.6×10^{-8} M. The low value obtained by GC was probably due to losses in the extraction procedure. The high value reported by AdSV was due to a small peak observed in the blank environmental sample prior to spiking. If this blank peak was taken into account, a value of 7.4×10^{-8} M was obtained. Obviously, "blank peaks" cannot be accounted for in this mannner. In the absence of an effective clean-up procedure, this electrochemical technique should be limited to relatively "clean" environmental samples, e.g. wellwater, springwater, "clean" freshwater rivers, etc.

It was noted that the six pesticides which demonstrated accumulative properties all contained sulfur atoms. In addition, mercury affinity for sulfur is well-known.[21,22] To better understand if this Hg-S affinity is playing a role, analysis by AdSV of Simazine was attempted. Simazine is the chloro analog of the methylthio *s*-triazine Simetryne. No such accumulation was noted for Simazine, lending support to the suggestion that Hg-S affinity is at least partly responsible for adsorption of these pesticides onto the electrode surface. Even though compounds not containing sulfur are amenable to analysis by AdSV,[10,11] its presence in these pesticides seems to be significant with respect to adsorption.

In conclusion, it can be seen from results described herein that six sulfur-containing pesticides can be analyzed sensitively by AdSV, with an increase in sensitivity over DPP by a factor of 20–50. Three of these pesticides could be analyzed while present in the same solution. The method was found to be applicable to several fresh water environmental samples. Co-adsorbants were found to interfere only when present at high concentrations or when the co-adsorbant gave interfering peaks in the stripping voltammogram. When present at low to moderate concentrations, co-adsorbants appeared simply to decrease the sensitivity of the technique. Pesticide-adsorbing colloids could interfere in "total" pesticide concentration determinations. However, the technique potentially could be used as a speciation tool in determining "free" pesticide concentrations. The technique is best applied to relatively clean environmental samples. In samples containing high concentrations of either co-adsorbants or adsorbing colloids, a clean-up procedure should be envisaged.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC Grant No. A1938) and by the Conseil de la Recherche de l'Université de Moncton. M.D. wishes to acknowledge support from NSERC in the form of a postgraduate scholarship.

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