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THE FEASIBILITY OF USING SOLID SORBENT PACKED MINITUBES
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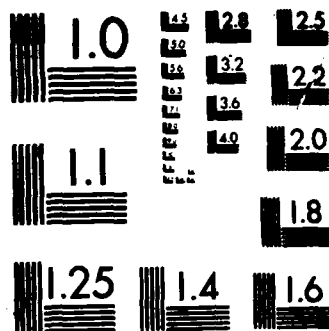
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SUFFIELD MEMORANDUM

NO. 1186

THE FEASIBILITY OF USING
SOLID SORBENT PACKED MINITUBES
FOR THE ANALYSIS OF AQUEOUS ORGANICS (U)

by

J.R. Hancock
and
M. Totland

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Abstract

A study was conducted to determine the feasibility of analyzing trace levels of organics in water, by adsorption onto a solid sorbent packed minitube followed by thermal desorption-gas chromatographic analysis. The study included: selecting appropriate sorbents, determining the optimum thermal desorption temperature, performing wet/dry experiments, choosing the optimum drying conditions and measuring analyte breakthrough (or capacity) of the minitubes. Experimental results with methyl salicylate and Chromosorb 102 yielded breakthrough volumes in excess of 50 milliliters, indicating that this could be an extremely sensitive method for the analysis of organics in water.

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Introduction

1. Methods which exist for the analysis of trace amounts of organics in water, include: solvent extraction, direct injection onto a chromatographic column and absorption onto a solid support followed by either solvent elution or thermal desorption.
2. Solvent extraction can be a time-consuming and cumbersome technique, requiring large sample volumes in addition to pure solvents. Changes in the extracting solvent may result in different quantitative and qualitative extraction efficiencies (1,2). Methods involving direct injection on to a chromatographic column usually lack sensitivity. In addition, water destroys many stationary phases and makes some types of detection, like electron capture, difficult (3).
3. Solid adsorbents offer the potential of sample clean-up and preconcentration in one step. Absorption onto a solid support followed

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by solvent elution has found wide applications (2,4,6,8,9). This technique, however, has many of the same solvent related problems as liquid-liquid extractions. Adsorption onto a solid support, followed by thermal desorption, permits analysis of compounds of intermediate to high volatility (2,3,10,11,12). This method requires no solvents and has maximum sensitivity because all the adsorbed organics can be desorbed onto a gas chromatographic (GC) column.

4. Solid sorbents frequently used in a preconcentration step are: activated charcoal, silica gel, alumina, molecular sieves, graphitized carbon black and porous polymers. The initial selection of sorbent packings for this study was influenced by the current scientific literature. The criteria used to select a packing were: low affinity for water, thermal stability up to 250°C and good capacity and recovery of organics.

5. Carbopack B, a partially graphitized carbon black, was chosen as a representative carbon sorbent. It has been reported that Carbopack B does not give rise to sampling artifacts in the presence of oxidants and acidic pollutants as do some porous polymers (5). Care must be taken to ensure complete recovery of organics from Carbopack B, since some carbon-based adsorbents retain many organics and catalyze their degradation (3).

6. Porous polymers have found extensive application in the preconcentration of organics because of their chemical inertness, minimum adsorption of water and high affinity for organics (7). Sorbent packings which have been studied include the Amberlite XAD series, the Chromosorb series and Tenax GC. Most of the studies on these compounds employed adsorption onto the solid support, followed by solvent elution. In the Amberlite XAD series, all but XAD-7 will be considered.

Amberlite XAD-7 is a methacrylate polymer which has a hydrophilic structure making it unsuitable for water analysis (2). Chromosorb 102 was chosen from the Chromosorb series as it has the highest upper temperature limit. The upper temperature limit is defined as the maximum temperature at which the chromatographic background of the sorbent is acceptable from the analytical viewpoint (2). Tenax GC, (2,6-diphenyl-p-phenylene oxide), is commonly used in air and water sampling. It is stable at high temperatures, has low blank levels for thermal desorption and a high affinity for a wide variety of non-polar organics (3).

7. The Canadian Center for Advanced Instrumentation (CCAI) and DRES have developed a system to analyse organics in air: the Minitube Air Sampling System (MASS). This is an integrated system for adsorbing volatile organics, from air, onto a sorbent packed minitube (2 mm ID x 38 mm) followed by thermal desorption onto a GC column (13). The possibility exists that components of this system could be applied to water sampling and analysis.

8. The objective of this study was to determine the feasibility of using solid sorbent packed minitubes and thermal desorption gas chromatography (TD/GC) for the analysis of organics in water. In order to properly evaluate this technique a number of protocols were established.

9. Parameters which were considered included the selection of an appropriate sorbent material, establishing the optimum thermal desorption temperature of the packings, determining drying conditions for the tube, and measuring the breakthrough (or capacity) of the tube.

Experimental

Apparatus

10. The gas chromatograph used in this study was a Varian 6500. The instrument conditions were as follows:

Carrier gas:	Helium
Carrier flow rate:	30 mL/min
Detector:	FID at 240°C
Injector:	Thermal desorption unit
Column:	Glass 4 ft. x 1/8 in.
Stationary Phase:	10% SP-1000 on Supelcoport 80/100 mesh

11. The injection system was a prototype thermal desorption unit (TDU) developed by CCAI. The TDU inserts a minitube into a preheated oven, carrier gas is then passed through the minitube and sweeps the desorbed volatiles onto the column. The TDU is microprocessor controlled, giving the operator control of desorption temperature (isothermal or temperature programmed) analysis time and initial and final minitubes. These parameters can be entered from a keypad on the instrument or from a pre-programmed EPROM.

12. A Nelson Analytical Model 6000 Data System was used for all chromatographic data acquisition, processing and reporting.

Sorbent materials

13. For this study, individual minitubes were hand-packed with each of the following sorbent packings: Amberlite XAD-2, XAD-4, XAD-8,

Carbopack B, Chromosorb 102 and Tenax GC. Each tube was tested to ensure the pressure drop was within the allowable limits of the MASS. A problem arose with Carbopack B. When the tube was packed with the same volume of Carbopack B as the other packings, it acted as a restrictor in the chromatographic system which exceeded the ability of the GC to keep a constant flow of carrier gas. In order to eliminate this problem, a reduced volume of Carbopack B was used. Table 1 is a summary of the sorbent materials used.

Table 1
Selected Physical Properties
of the Sorbent Materials

Adsorbent	Supplier	Mesh Size	Amount Adsorbent per tube (mg)
Amberlite XAD-2	BDH Chemicals Canada	20-50	27
Amberlite XAD-4	BDH Chemicals Canada	20-50	32
Amberlite XAD-8	BDH Chemicals Canada	20-50	20
Carbopack B	Supelco Inc.	60-80	7.2
Chromosorb 102	Chromatographic Specialties Inc.	80-100	21
Tenax GC	Alltech Associates	60-80	12

Adsorption-Desorption Procedure

14. Two techniques were used to load the minitubes. These were adsorption of the analyte from a vapour or from water.
15. For compounds adsorbed onto minitubes from vapour, a modified packed column GC injection port, with a teflon liner, was used. The modifications included external temperature control and a teflon fitting machined to allow a minitube to be press-fit into the injection port. The sample solution was introduced into the injection port using a microlitre syringe where it was vaporized and nitrogen used to sweep the volatilized solvent and analyte onto the minitube.
16. Adsorption from an aqueous media required a different technique. A syringe pump (Sage, Model 355, Orion Research Incorporated) was used to supply a constant, pulse free, flow of liquid. Short pieces of teflon tubing were used to attach the minitubes to the syringe pump. Care was taken to minimize dead-volume in these connections.
17. After passing the desired volume of water through a minitube, it was dried (at room temperature) in a flow of nitrogen. Drying times in the range of 5-15 minutes and flowrates of 100-200 mL/min were investigated. Teflon tubing was used to connect the minitube to the regulator of the gas cylinder.
18. Desorption of the minitubes, after both vapour and water adsorption, was carried out using the TDU. The loaded minitubes were inserted into a MASS carousel which was then loaded into the TDU. The desorption conditions depended on which test was being performed.

Results and Discussion

Selection of Analyte and Sample Matrix

19. In order to evaluate the potential of sorbent packed minitubes and thermal desorption-gas chromatography for the analysis of aqueous organics it was necessary to select a target compound and the sample matrix. For this study, methyl salicylate, a simulant for mustard, was chosen as the analyte. Water can be obtained from many sources and each type of water may contain varying amounts of background material. Pond surface water was chosen as representative of a real sampling environment. The water contained a large number of suspended particulates and was initially filtered through glass wool, and finally through Millipore glass microfiber filters.

20. The initial selection of sorbent packings included: Amberlite XAD-2, XAD-4, XAD-8, Carboxpack B, Chromosorb 102 and Tenax GC. In order to reduce the number of sorbents three performance characteristics were evaluated. These were: the thermal desorption profile, the recovery of adsorbed compounds and the physical appearance of the sorbent after use.

21. The thermal desorption profile was obtained by running two consecutive thirty minute desorptions of each tube. Figures 1 through 6 show the GC/FID chromatograms of the thermal desorption profiles of each packing. They show the initial background level as well as how effective thermal desorption was at reducing the background. For comparison purposes, each chromatogram was run under the same conditions: isothermal at 200°C and a desorption temperature of 180°C. From Figures 1, 2, 3 and 5 it can be seen that a large amount of material is

removed from XAD-2, XAD-4, XAD-8 and Chromosorb 102 during the first desorption. There is much less material desorbed from Carbopack B and Tenax GC. For all six packings, the chromatograms of the second desorption show a reduction in the amount of volatiles. For Amberlite XAD-8 and Chromosorb 102, the level of volatiles after the second desorption was still too high. With a desorption temperature of 180°C, Chromosorb 102 could be cleaned with three desorptions. Amberlite XAD-8 had an elevated baseline even after multiple desorptions.

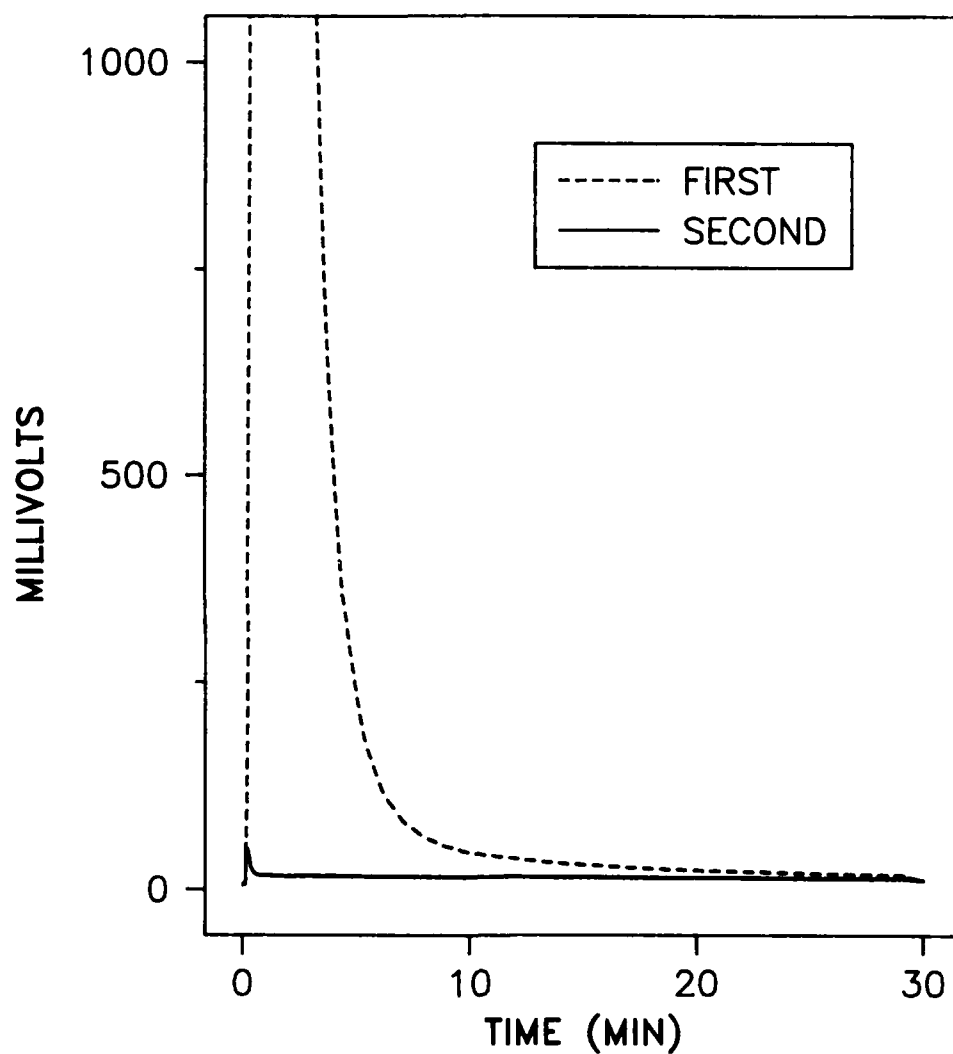


FIGURE 1. TWO CONSECUTIVE THERMAL DESORPTIONS OF AN AMBERLITE XAD-2 MINITUBE. PACKED COLUMN GC, ISOTHERMAL AT 200°C, WITH FID DETECTION, THERMAL DESORPTION TEMP 180°C.

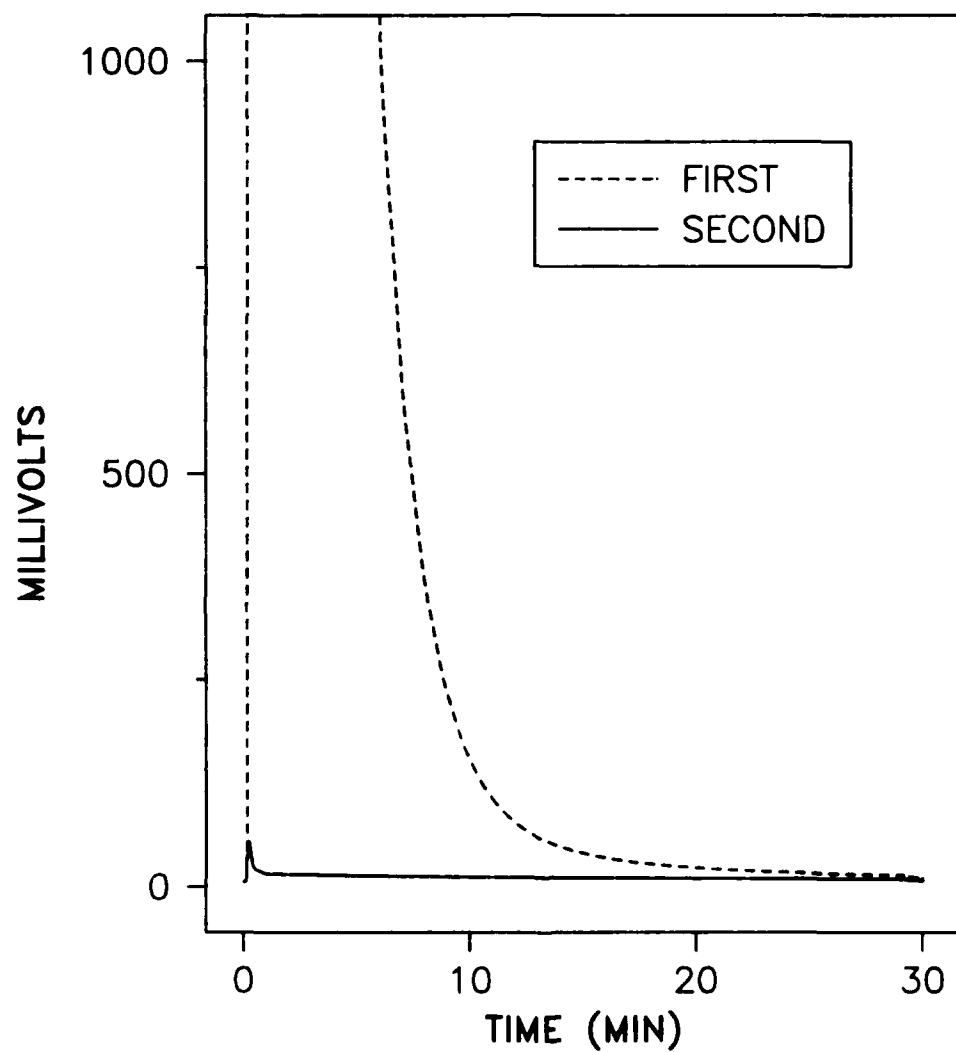


FIGURE 2. TWO CONSECUTIVE THERMAL DESORPTIONS OF AN AMBERLITE XAD-4 MINITUBE. PACKED COLUMN GC, ISOTHERMAL AT 200°C, WITH FID DETECTION, THERMAL DESORPTION TEMP 180°C.

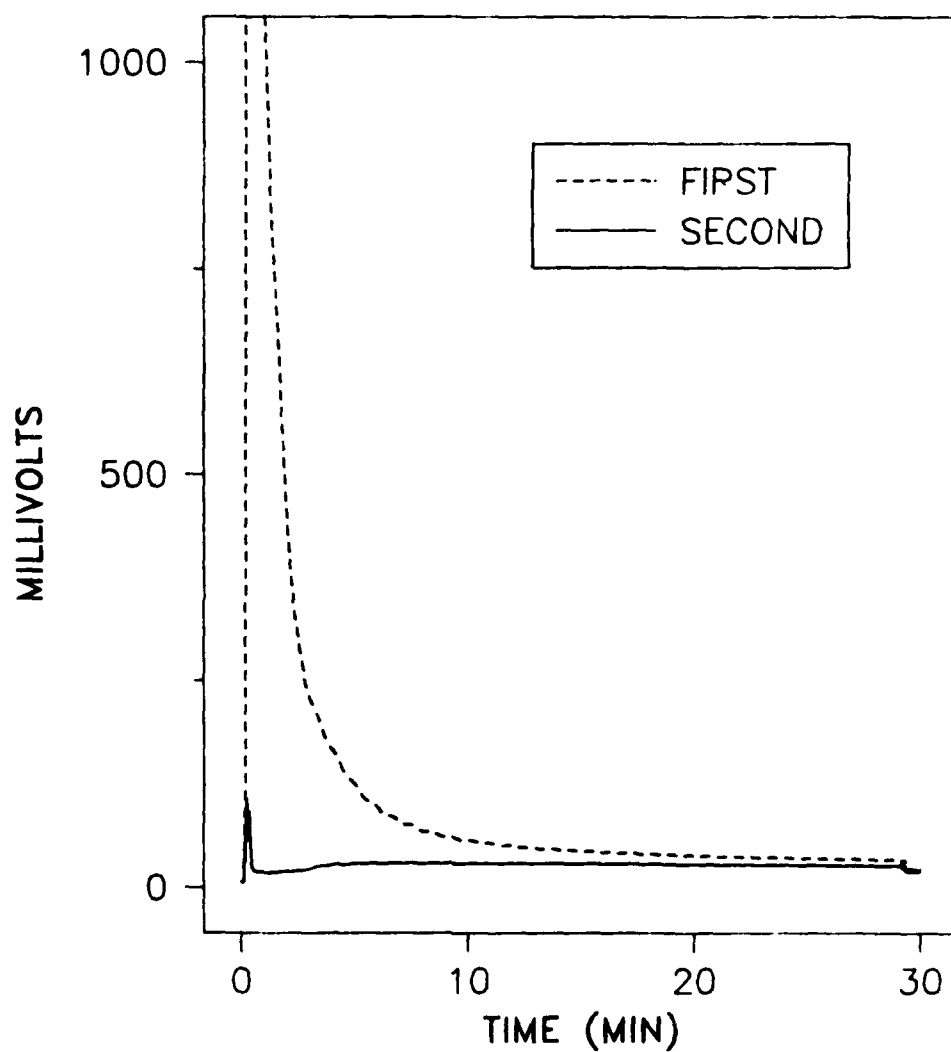


FIGURE 3. TWO CONSECUTIVE THERMAL DESORPTIONS OF AN AMBERLITE XAD-8 MINITUBE. PACKED COLUMN GC, ISOTHERMAL AT 200°C, WITH FID DETECTION, THERMAL DESORPTION TEMP 180°C.

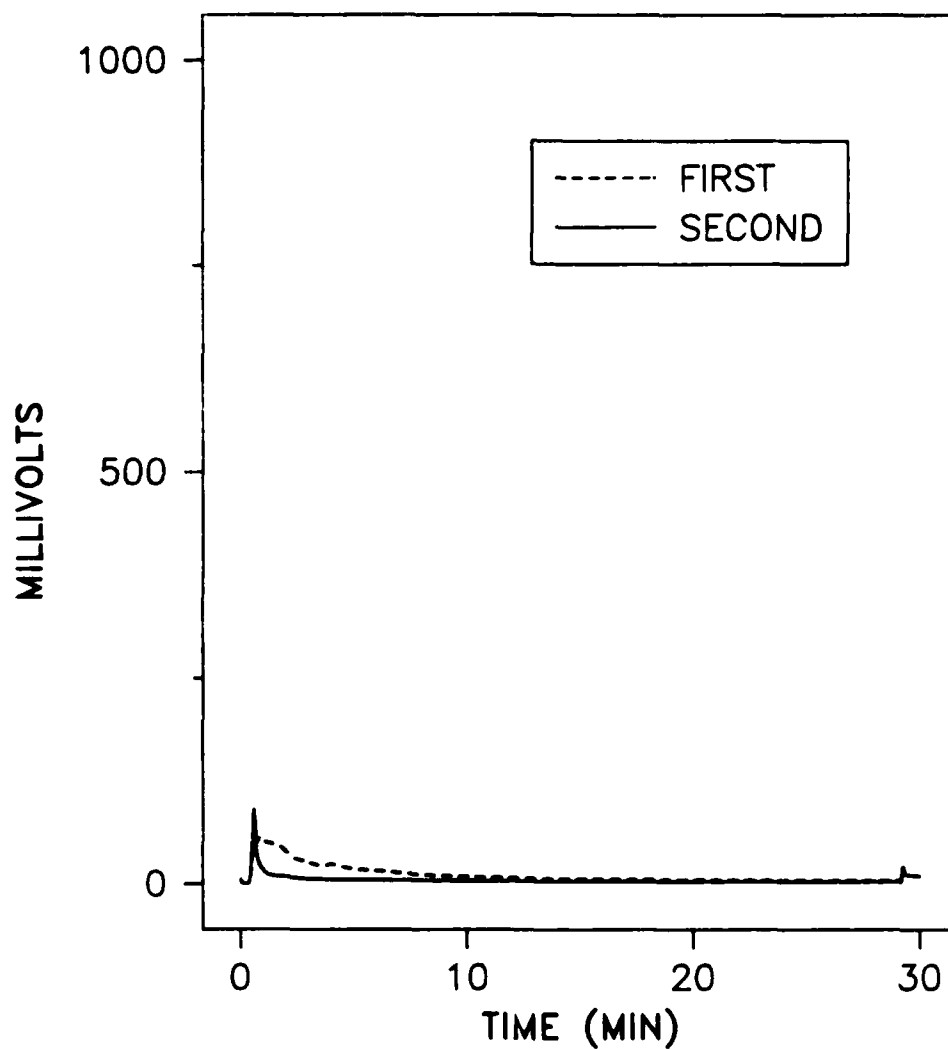


FIGURE 4. TWO CONSECUTIVE THERMAL DESORPTIONS OF A CARBOPACK B MINITUBE. PACKED COLUMN GC, ISOTHERMAL AT 200°C, WITH FID DETECTION, THERMAL DESORPTION TEMP 180°C.

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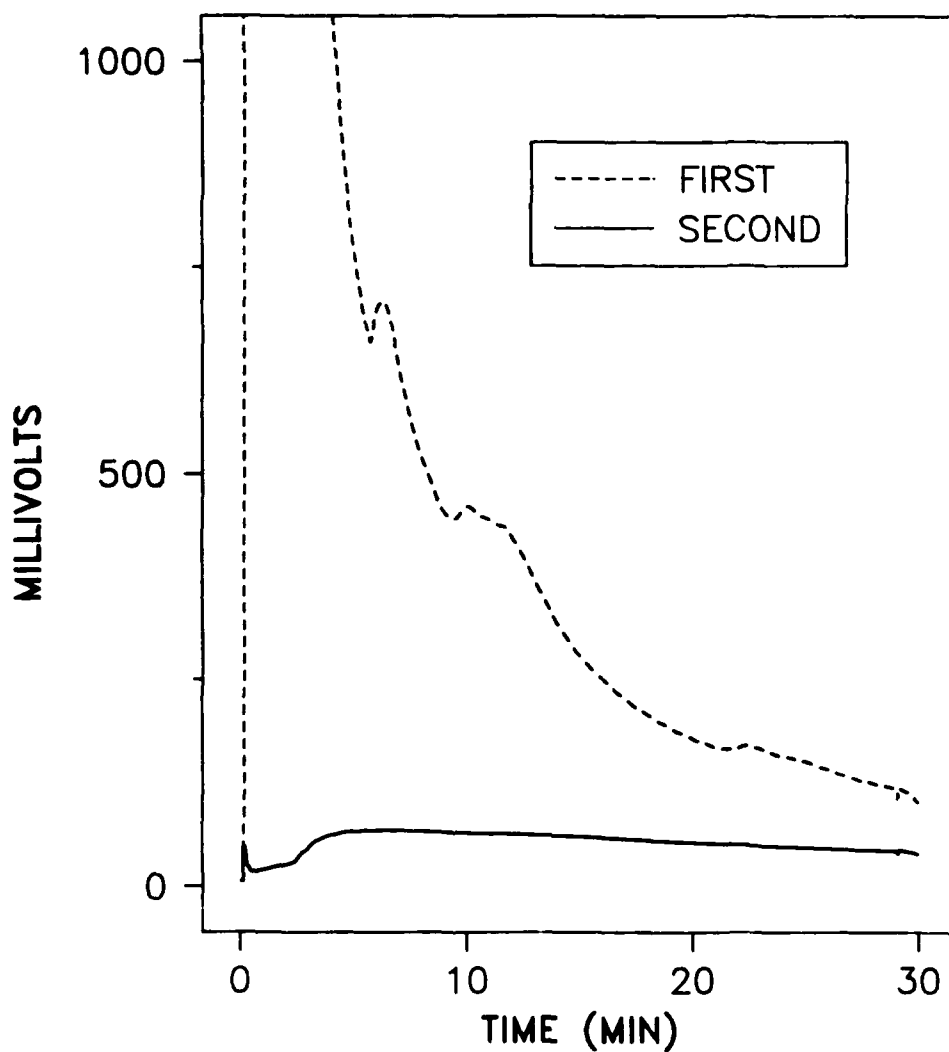


FIGURE 5. TWO CONSECUTIVE THERMAL DESORPTIONS OF A CHROMOSORB 102 MINITUBE. PACKED COLUMN GC, ISOTHERMAL AT 200°C, WITH FID DETECTION, THERMAL DESORPTION TEMP 180°C.

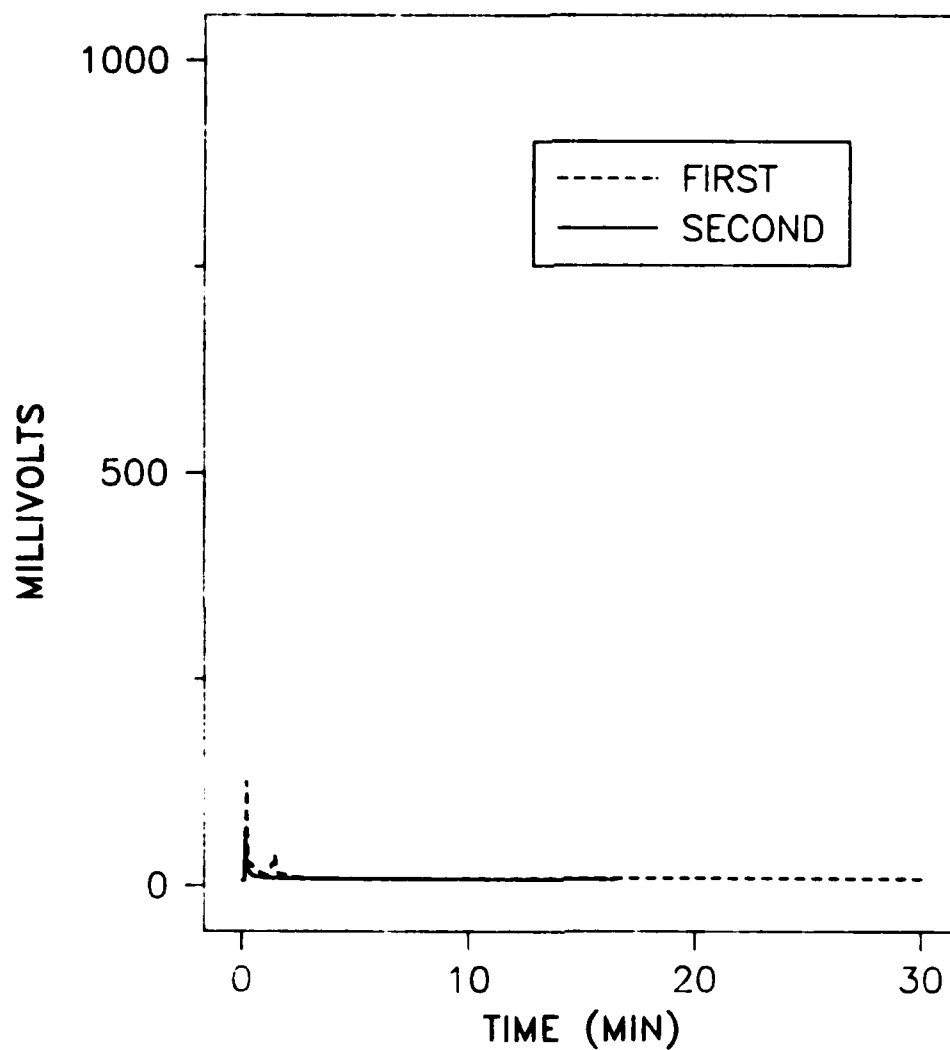


FIGURE 6. TWO CONSECUTIVE THERMAL DESORPTIONS OF A TENAX GC MINITUBE. PACKED COLUMN GC, ISOTHERMAL AT 200 °C, WITH FID DETECTION, THERMAL DESORPTION TEMP 180°C.

22. Methyl salicylate was used to evaluate the ability of the adsorbents to desorb an analyte. Each minitube was loaded, using the vapor method, with 118.5 ng of MS. A range of temperatures, between 160°C and 240°C, was used for thermal desorption, with packings being tested at either 3 or 4 temperatures. The average MS peak area for each adsorbent is presented in Table 2. Assuming Tenax has a recovery of 100%, Table 2 gives a relative comparison of the recovery from each sorbent material.

Table 2

The Average Peak Area for 118.5 ng
MS Over a Range of Desorption Temperatures

Sorbent Material	MS Peak Area (counts in 1000's)	% Recovery vs Tenax GC
Amberlite XAD-4	331	60
Amberlite XAD-8	340	62
Amberlite XAD-2	441	80
Chromosorb 102	505	91
Carbopack B	534	97
Tenax GC	553	100

23. A change in appearance of a tube after thermal desorption may indicate a change in its performance characteristics. The originally white XAD-4 resin showed yellowing after a few desorptions as well as

melting along the glass wall of the tube. The opaque XAD-8 became clearer after thermal desorption. The appearance of the other adsorbents was unchanged following thermal desorption.

24. Following the thermal desorption profile, recovery and appearance tests, Amberlite XAD-2, Chromosorb 102, Carbopack B and Tenax GC were selected for further testing.

Chromatographic Background Associated with Pond Water

25. Five milliliters of pond water was passed through a minitube packed with one of the chosen adsorbents and analysed by TD/GC/FID. Figures 7-10 show these chromatographs. The chromatograms for all the packings appear similar, showing a number of early eluting peaks at a GC column temperature of 150°C, the analysis temperature for MS on an FFAP column. Different column conditions can be used to ensure the peaks don't interfere with the analyte peak. Pond water can therefore be used as the media for aqueous organics and will make the performance tests more realistic in terms of interferences from other organics.

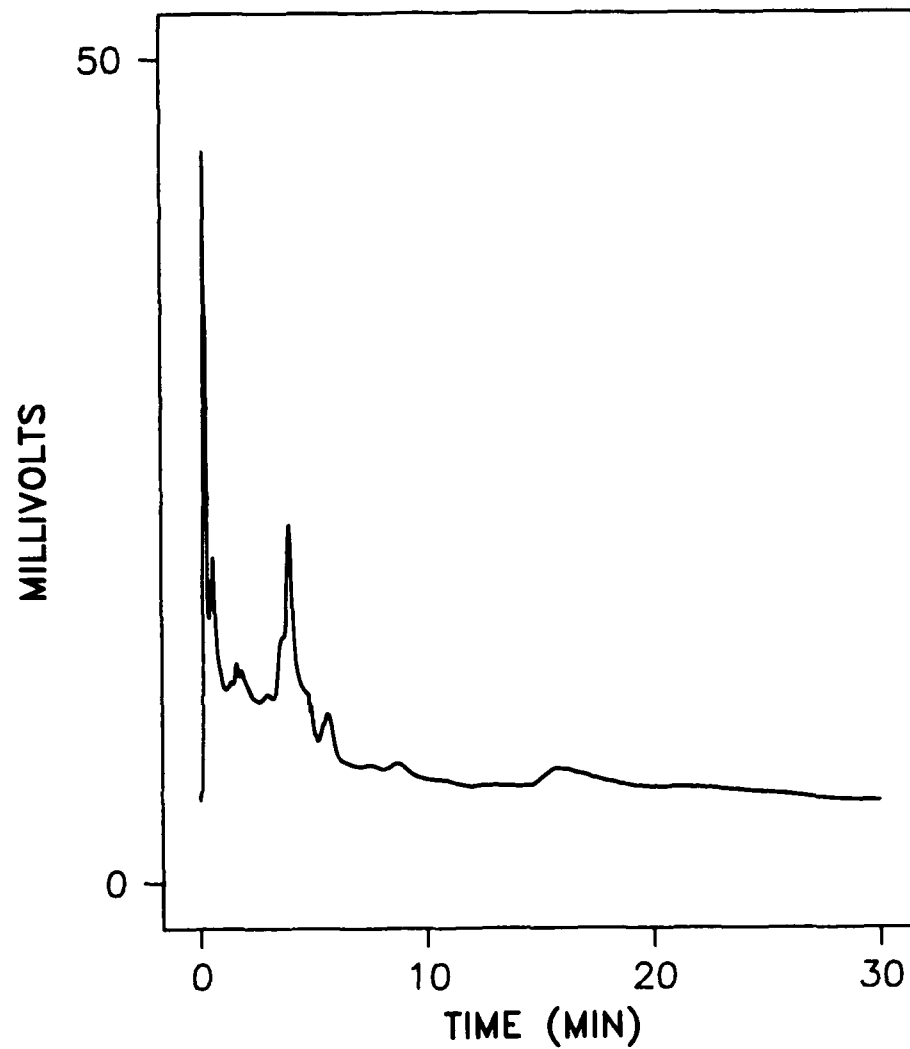


FIGURE 7. POND WATER AS BACKGROUND ON AMBERLITE XAD-2. PACKED COLUMN ISOTHERMAL AT 150°C, FID DETECTION. DESORPTION TEMPERATURE 180°C.

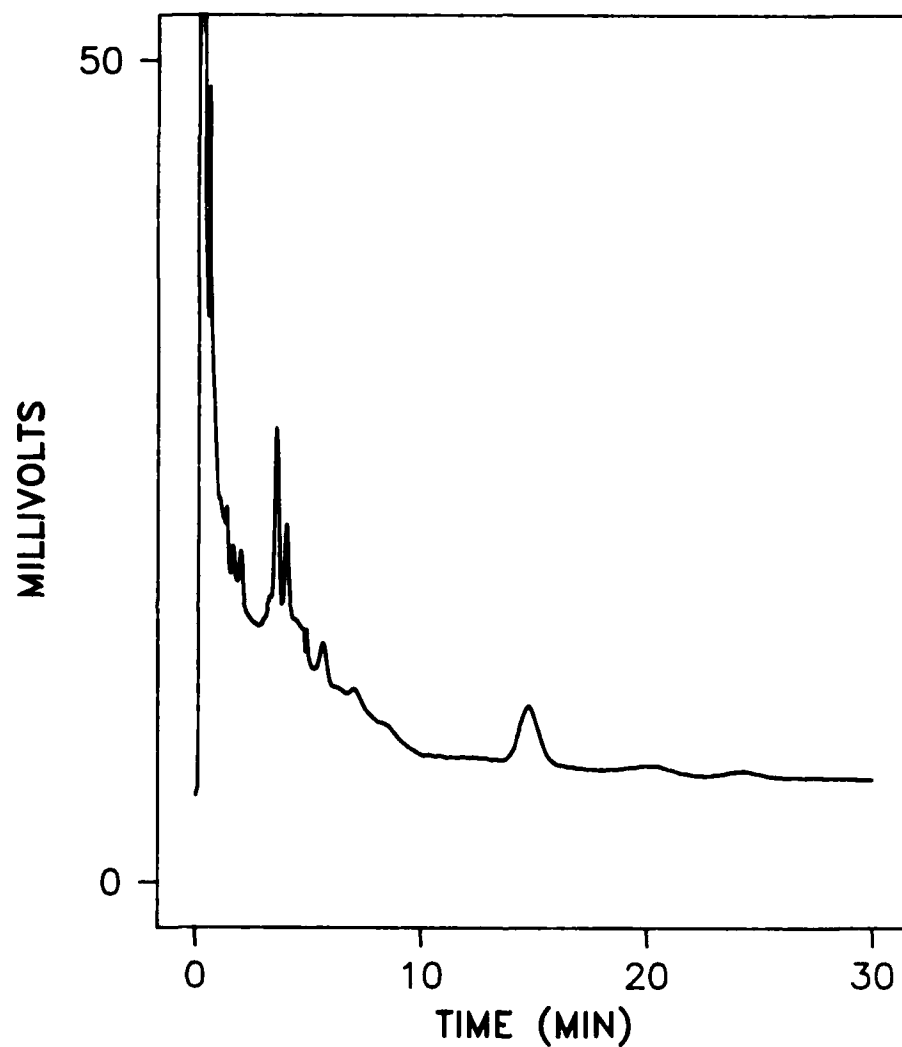


FIGURE 8. POND WATER AS BACKGROUND ON CARBOPACK B.
PACKED COLUMN GC, ISOTHERMAL AT 150°C,
FID DETECTION, DESORPTION TEMPERATURE 180°C.

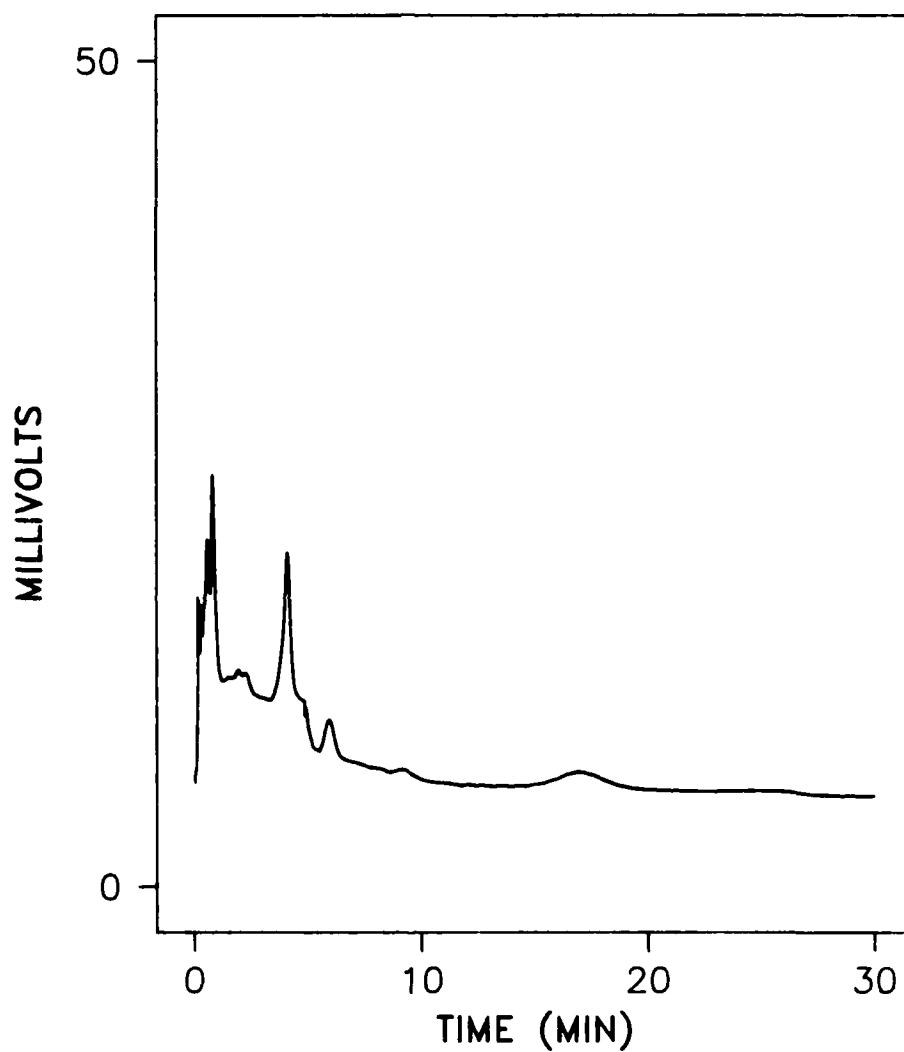


FIGURE 9. POND WATER AS BACKGROUND ON CHROMSORB 102.
PACKED COLUMN GC, ISOTHERMAL AT 150°C,
FID DETECTION, DESORPTION TEMPERATURE 180°C.

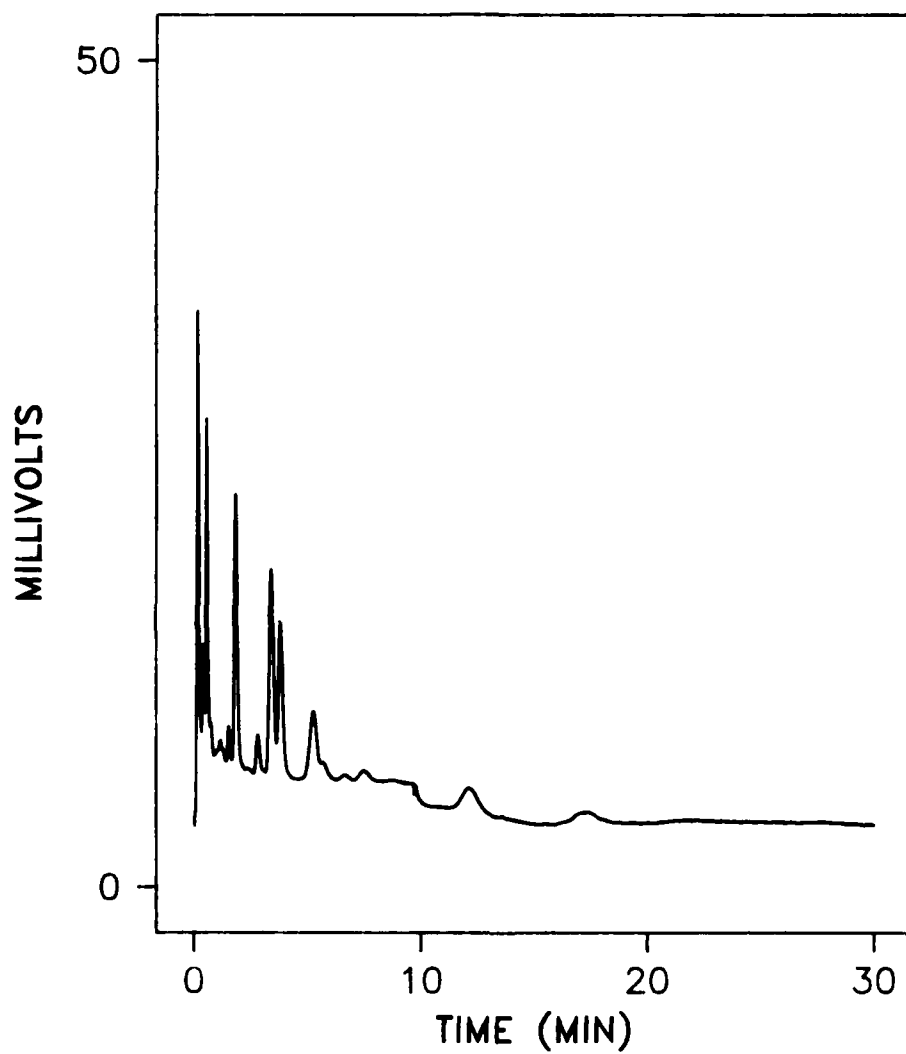


FIGURE 10. POND WATER AS BACKGROUND ON TENAX-GC.
PACKED COLUMN GC, ISOTHERMAL AT 150°C,
FID DETECTION, DESORPTION TEMPERATURE 180°C.

Proof of Concept

26. The initial stages of this project involved selecting the target compound and sample matrix. Next the adsorbents were evaluated and finally the background associated with the pond water has been investigated.

27. The next step was to prove that the concept of adsorption onto minitubes, followed by the thermal desorption gas chromatographic analysis was viable. Chromosorb 102 was selected from the list of adsorbents for the test. It was chosen over XAD-4 due to its higher recovery of methyl salicylate. Carbopack B was not selected as there was concern over the optimum desorption temperature. Chromosorb 102 was chosen over Tenax-GC as Tenax has been used extensively in MASS and experience with a new adsorbent was considered desirable.

28. A 2 mg/L standard of methyl salicylate in pond water was used to challenge the Chromosorb 102 packed minitube. In total, 2 mL of water was passed through the minitube, which was then dried in a stream of nitrogen and analyzed by TD/GC. Figure 11 shows the thermal desorption-gas chromatographic analysis of methyl salicylate. Although the MS peak tails due to interaction with the stationary phase, peak shape and width were considered to be very good.

29. Having shown that the concept was viable, the following experiments were conducted to determine the overall feasibility of this approach: optimum thermal desorption temperature, wet/dry tests and measurement of analyte breakthrough.

Thermal Desorption Temperature

30. From previous experience with thermal desorption, it had been observed that the desorption temperature affected peak shape, peak area

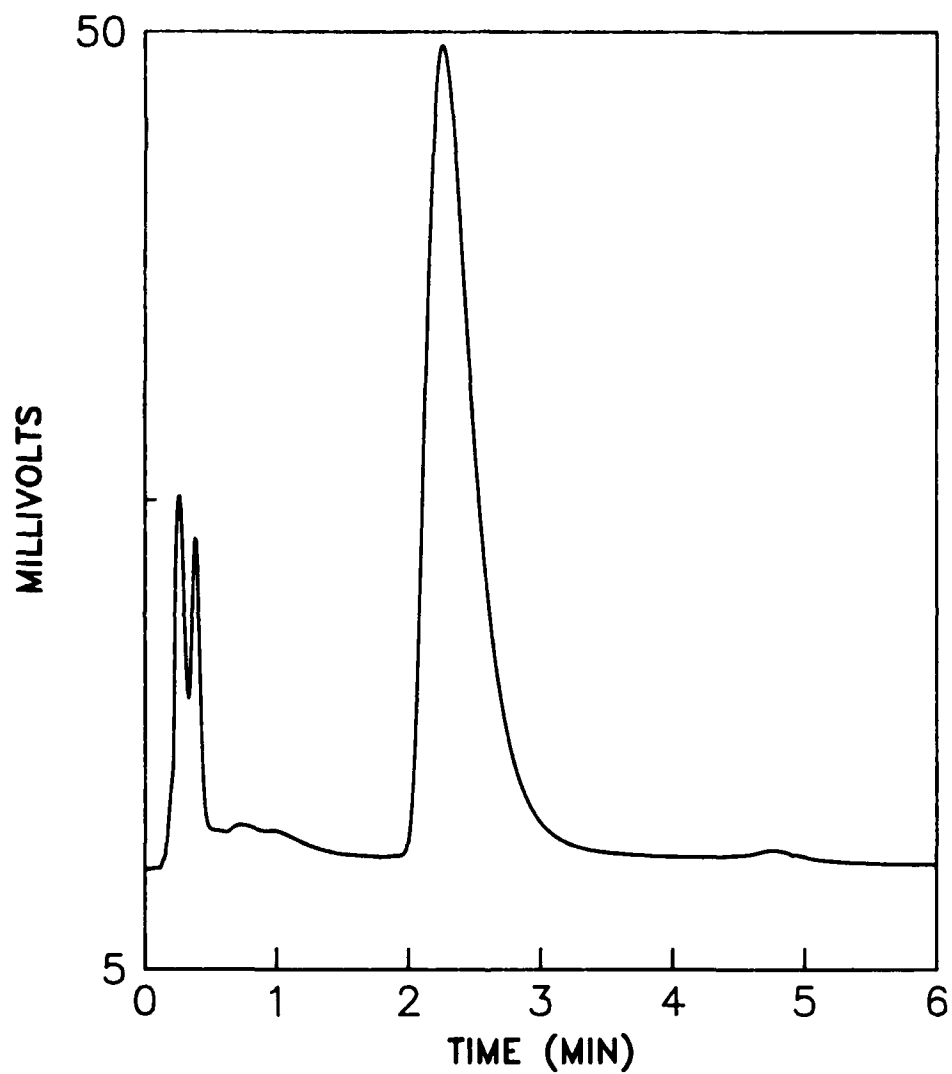


FIGURE 11 METHYL SALICYLATE (~4ug) ON A CHROMOSORB 102
MINITUBE, PACKED COLUMN GC, ISOTHERMAL AT 150°C, FID
DETECTION, DESORPTION TEMPERATURE 180°C.

and retention time of some compounds. The optimum thermal desorption temperatures were determined by evaluation of peak shape over a range of temperatures. Figure 12 shows the chromatograms of methyl salicylate on Chromosorb 102 with desorption temperatures of 160°, 180° and 200°C.

31. There is an improvement in peak shape and height between the desorption temperatures of 160° and 180°C. There is very little difference between the 180° and 200°C chromatograms, implying an optimum peak shape can be obtained. Table 3 summarizes the retention times and peak areas for the three temperatures. There is no significant change in retention time between the temperatures. A desorption temperature of 200°C was considered optimal.

Table 3

Retention Time and Peak Area for MS
on Chromosorb 102 at Various Desorption Temperatures

Desorption Temp. (°C)	Retention Time (min)	Peak Area (counts in 1000s)
160	2.569	481
180	2.567	505
200	2.579	530

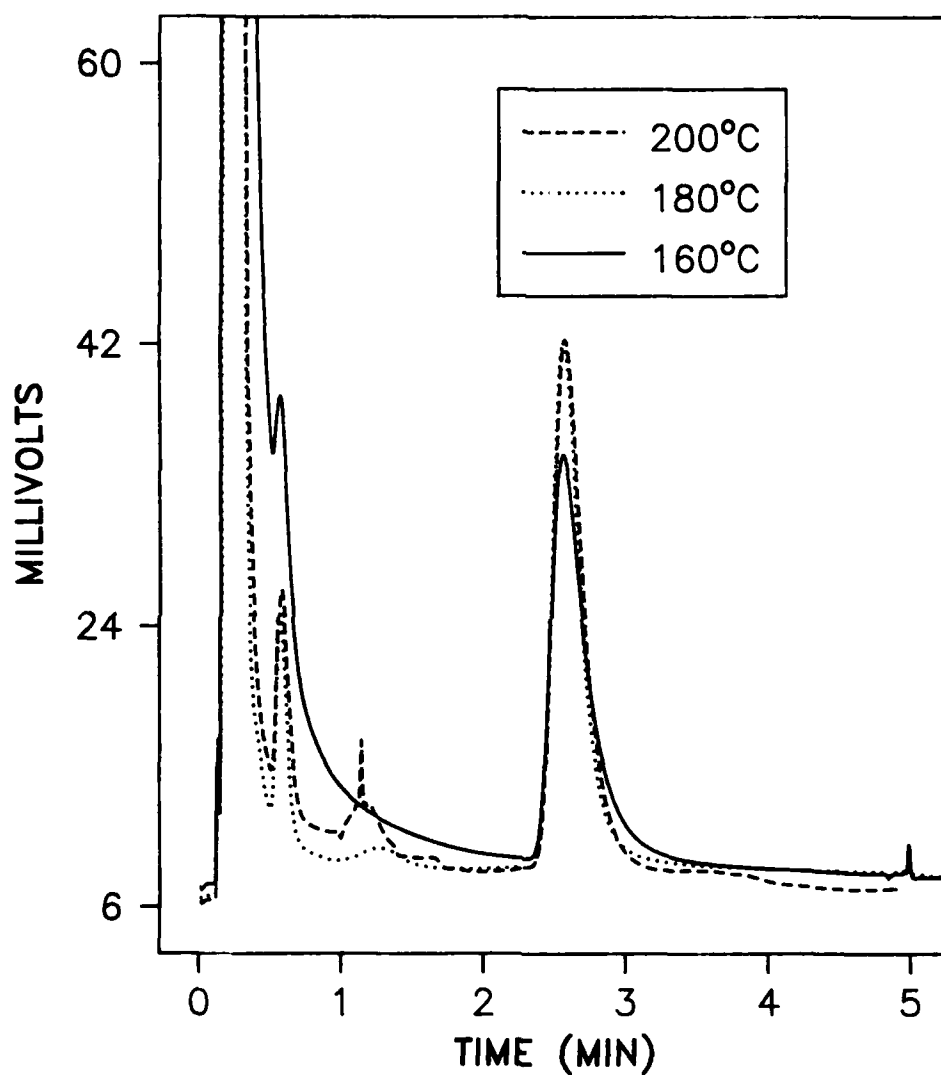


FIGURE 12. THERMAL DESORPTION OF METHYL SALICYLLATE
ON CHROMOSRB 102. PACKED COLUMN GC,
ISOTHERMAL AT 150°C, FID DETECTION
DESORPTION TEMPERATURES: 160°, 180° AND 200°C

Wet/Dry Test

32. While working with tubes packed with dry Chromosorb 102, it was noticed that initially some MS passed through the tube and was not adsorbed. Wetting the tube by passing 2 mL distilled water through the tube, before the MS spiked water, almost eliminated the problem. An experiment was done in which 2 mL of 2 mg/L MS in surface water was passed through two Chromosorb 102 minitubes connected in series to the syringe pump. The two tubes were then analysed and averages from triplicate runs with dry tubes and wetted tubes were calculated. Table 4 shows the results from this test on Chromosorb 102 with MS. The average area for MS on the second tube of the dry test was 20% of the average total area of MS from both tubes. There was only 0.2% MS on the second tube from the wetted tubes.

Table 4Wet/Dry Results for Methyl Salicylate on Chromosorb 102

	Dry Tube		Wet Tube		
	MS peak area first tube (counts)	MS peak area second tube (counts)	MS peak area first tube (counts)	MS peak area second tube (counts)	Total MS Peak Area (counts)
trial 1	10 040 714	1 614 876			11 655 590
trial 2	10 583 488	2 013 757			12 597 245
trial 3	8 424 863	3 397 651			11 822 514
trial 1			12 269 902	59 833	12 329 735
trial 2			11 098 294	434	11 098 728
trial 3			11 073 359	13 428	11 086 787
average	9 700 000	2 300 000	11 500 000	20 000	11 800 000
standard deviation	1 100 000	940 000	700 000	30 000	600 000

Drying Conditions

33. The liquid phases used in packed gas chromatographic columns are typically sensitive to water; therefore a drying step was included before analysis. For simplicity, the tubes were purged in a flow of nitrogen. To ensure there was no loss of compound during this step, as well as to find the optimum N₂ flow rate and drying time, MS peak areas were measured at various drying conditions. Two flow rates 100 and 200 mL/min., and three drying times, 5, 10 and 15 minutes were chosen. Each condition was tested in triplicate and the averages are shown in Table 5.

Table 5

Average Methyl Salicylate Peak Area (counts) on
Chromosorb 102 with Various Drying Conditions

N ₂ Flow Rate	Drying Time		
	5 min	10 min	15 min
100 mL/min	visibly wet	1 200 000	1 200 000
200 mL/min	930 000	1 100 000	800 000

34. As seen in Table 5, drying the tube for five minutes at 100 mL/min left the tube visibly wet. To protect the GC column, this tube was not analysed. There is little difference between drying for 10 or 15 minutes at 100 mL/min but with a flow rate of 200 mL/min there is little consistency over the drying times. The peak areas are less with a flow rate of 200 mL/min, indicating a loss of MS during drying. A flow rate of 100 mL/min was chosen and the shortest time, 10 minutes, was chosen as the optimum drying conditions for MS and Chromosorb 102.

Breakthrough Test

35. Breakthrough volume is a measurement of the capacity of a sorbent for an analyte. Breakthrough is dependent on flow rate during adsorption, sample concentration, sorbent material and the analyte. The flow rate was set at approximately 0.5 mL/min and the MS concentration at 2 mg/L. Two tubes were connected to the syringe drive pump in series and the second tube was periodically analysed. Figure 13 shows the breakthrough curves for MS on three different Chromosorb 102 minitubes. The breakthrough curves are the percent MS accumulated on the second tube (relative to the total amount of MS passed through the first tube) versus the total volume of solution.

36. As seen in Figure 13, the three tubes show similar breakthrough curves. There is very little MS on the second tube for the first 50 to 75 mL followed by a sharp increase. It is expected that this increase will continue until the MS on the second tube is 100% of the amount passed through the first tube; i.e. saturation of the first tube has occurred. Although a precise breakthrough volume was not calculated, it is clearly in excess of 50 mL at this concentration.

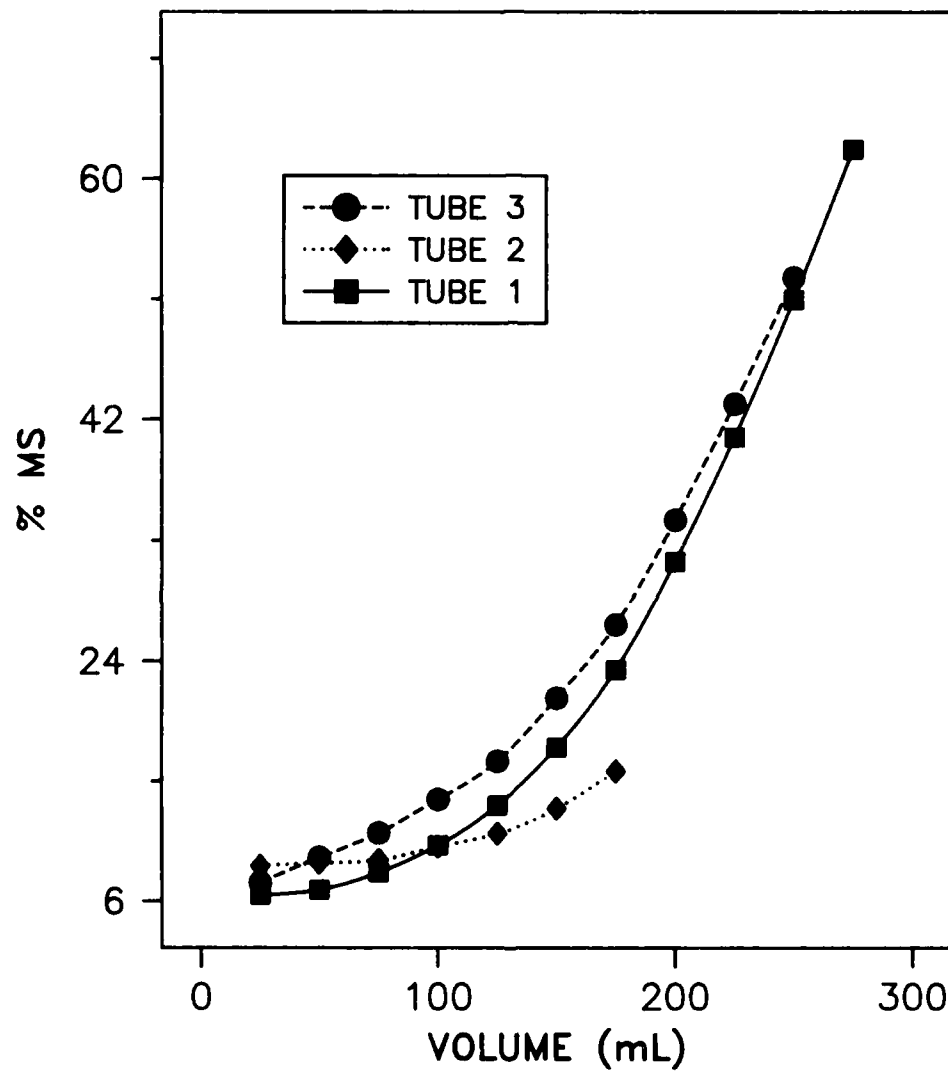


FIGURE 13. BREAKTHROUGH CURVES FOR MS ON CHROMOSORB 102. FLOWRATE 0.5 mL/min, MS CONCENTRATION 2 mg/mL.

Conclusions

37. This study involved the establishment of protocols to evaluate the feasibility of using solid adsorbent packed minitubes and thermal desorption gas chromatography as a method for the analysis of aqueous organics.

38. Although absolute sensitivity was not determined, the limiting factor appears to be the sensitivity of the chromatographic detector. Breakthrough volumes for 2 mg/L aqueous solutions of methyl salicylate on Chromosorb 102 for MS are in excess of 50 mL and the capacity of Chromosorb 102 is greater than 4 µg. When these factors are considered, the use of solid adsorbents and thermal desorption potentially offers an extremely sensitive method for the analysis of organics in water.

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