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APPLICATIONS OF A HIGH PRESSURE SOXHLET EXTRACTOR USING LIQUID CO_2 FOR THE EXTRACTION OF ORGANIC PHOSPHONATES FROM SOLID ADSORBENTS

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The feasibility and efficiency of extraction of various organic phosphonates from different adsorbents was studied using a soxhlet extractor enclosed in a stainless steel canister. Liquid CO_2 was used as the solvent. The CO_2 was introduced into the sealable cylinder, and the entire unit was pressurized by vaporizing the CO_2 with slight heating, and condensing the vaporized CO_2 on a cold finger.

14. SUBJECT TERMS

Tenax GC
Maxsorb
Absorbents
Activated charcoal
Trimethyl phosphate
Soxhlet extractor
Pinacolyl Alcohol
Triethyl phosphate
Chromosorb 108
Dimethyl methylphosphonate
Diisopropyl methylphosphonate
Diethyl methylphosphonate
Nomex polymer

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PREFACE

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CONTENTS

1. INTRODUCTION 7

2. EXPERIMENTATION 8

2.1 INSTRUMENTATION AND EQUIPMENT 8

2.2 MATERIALS 8

2.3 GENERATOR SET-UP/PROCEDURE 9

2.3.1 ESTABLISHING CALIBRATION CURVES 9

2.3.2 CHROMOSORB 108 15

2.3.3 ACTIVATED CHARCOAL, FISHER C277-350, LOT #904763, 6-12 MESH 15

2.3.4 KANSAI SUPERACTIVATED CARBON (MAXSORB, LOT #580A, 50% WATER) 15

2.3.5 MAXSORB II (ACTIVATED CHARCOAL AS IN SECTION 2.3.4) 15

2.3.6 MAXSORB III (ACTIVATED CHARCOAL AS IN SECTION 2.3.4) 18

2.3.7 CHROMOSORB 108/NOMEX POLYMER 18

2.3.8 TENAX GC/NOMEX POLYMER 3:1 RATIO #6669-30 22.3% SOLIDS . 18

2.3.9 ANDERSON CARBON/NOMEX POLYMER 3:1 RATIO #1041-46 18

3. CONCLUSION 21

3.1 DISCUSSION 21

3.2 EXTRACTION EFFICIENCY 21

4. FUTURE RESEARCH 21

LITERATURE CITED 23

FIGURES

1. Internal View of Soxhlet Extractor 10
2. Working Diagram of Soxhlet Extractor 11
3. Calibration Curve for Pinacolyl Alcohol 12
4. Calibration Curve for TMPO 12
5. Calibration Curve for DEMP 13
6. Calibration Curve for DMMP 13
7. Calibration Curve for DIMP 14
8. Calibration Curve for TEPO 14

TABLES

1. Chromosorb 108 16
2. Activated Charcoal, Fisher C277-0350, Lot #904763 16
3. Kansai Superactivated Carbon 17
4. Maxsorb II (Superactivated Carbon) 17
5. Maxsorb III (Superactivated Carbon) 19
6. Chromosorb 108/Nomex Polymer 19
7. Tenax GC/Nomex Polymer 20
8. Anderson Carbon/Nomex Polymer 20

APPLICATIONS OF A HIGH PRESSURE SOXHLET EXTRACTOR USING LIQUID CO_2 FOR THE EXTRACTION OF ORGANIC PHOSPHONATES FROM SOLID ADSORBENTS

1. INTRODUCTION

The interest in this type of extraction arose out of the need to extract organic compounds from charcoal filter beds. Traditionally, it is difficult to effectively desorb and identify organic compounds from charcoal, due to their adherence and/or adsorbence to the charcoal, and possibly destroying labile compounds if heated to a high degree.

The method employed in this study uses a soxhlet extractor enclosed in a stainless steel canister.Carbon dixode is introduced into a sealable cylinder and the entire unit is pressurized by vaporizing the CO_2 with a heated water bath at 50^0 C. A cold finger condenses the vaporized CO_2 and the resulting liquid CO_2 fills the soxhlet apparatus containing the sample adsorbent. The liquid CO_2 is transferred to the collection flask where the CO_2 is vaporized leaving the extracted residue behind. The extraction cycle repeats until terminated.[1]

One advantage is the low temperature needed to cycle the solvent through the sample and thus avoid the loss of low boiling compounds. While the method is not identical to supercritical fluid extraction since the CO_2 critical temperature and pressure are not utilized, it does have an advantage over traditional soxhlet extraction in that large amounts of solvent are not employed and the CO_2 is evaporated off at the termination of extraction.

An added advantage of the CO_2 extractor is that a large amount of sample adsorbent can be extracted compared to a thermally desorbed adsorbent tube. In this study, one and one-half to two and one-half grams of sorbent were spiked with the compunds of interest. Samples from charcoal filters or beds with amounts up to ten grams can be desorbed for detecting trace amounts of analytes.

Porous polymers are noted for adsorbing a wide range of both, polar and non-polar organic compounds. Porous polymers are readily thermally desorbed at relatively low temperatures.[2]

It was desirable to compare desorption effectiveness of some typical adsorbents by means of high pressure soxhlet extraction. Charcoal was of particular interest because of the poor recoveries cited for charcoal by other desorption methods.[3]

The research described here is an additional effort to ascertain the desorption efficiency of selected adsorbents applied to organic phosphorus compounds, and their detection levels, using this technique.[4]

A range of concentrations of organic phosphorus compounds were spiked onto Chromosorb 108, Activated Charcoal, a wetted charcoal called "Maxsorb", Anderson Carbon with Nomex polymer, and Tenax GC with Nomex polymer.

2. EXPERIMENTATION

2.1 INSTRUMENTATION AND EQUIPMENT

Analyses were conducted using the following instruments and equipment:

- High Pressure Soxhlet Extractor (J & W Scientific Co., Folsom, CA.)
- HP 5890GC, with a DB-5, 30 meter x 0.25 mm x 0.25 um capillary column. (J & W Scientific Co., Folsom, CA.)
- HP 5970B Mass Spectrometer (HewlettPackard, Palo, CA).
- Cryfocusing unit (Tekmar-Dohrman, Cincinnati, OH)
- Water bath capable of maintaining +/- 1.0^{0}C.
- Ice bath capable of pumping water at 0^0 C.

2.2 MATERIALS

The following materials were used:

- Chromosorb 108
- Activated Charcoal, Fisher C277-350, Lot # 904763
- Wetted Charcoal listed as Maxsorb
- Anderson Carbon with Nomex Polymer (Ratio 3:1, # 1041-46)
- Tenax GC with Nomex Polymer
- Methanol (HPLC grade, Burdick and Jackson)
- Methylene chloride (Burdick and Jackson)
- Pinacolyl alcohol (Aldrich Chemical Co.)
- Dimethyl methylphosphonate (DMMP) (Aldrich Chemical Co.)
- Trimethyl phosphate (TMPO) (Aldrich Chemical Co.)
- Diethyl methylphosphonate (DEMP) (Aldrich Chemical Co.)
- Diisopropyl methylphosphonate (DIMP) (Aldrich Chemical Co.)
- Triethyl phosphate (TEPO) (Aldrich Chemical Co.)

2.3 GENERATOR SET-UP/PROCEDURE

The accompanying diagrams (Figure 1 and 2) shows the operation of the generator.The liquid CO_2 is conducted first through a purification filter containing activated charcoal.The introduction of carbon dioxide is terminated by manually closing the valve when the level of liquid carbon dioxide in the pressure chamber reaches a point corresponding to the proper working volume of liquid for the extractor. This is determined by the precise position of the adjustable Teflon sleeve on the filler tube (see Figure 2.) When the liquid reaches this level during the filling operation, the gas being vented from the outlet becomes white with entrained dry ice snow.

Prior to charging the unit with CO_2, 1.5 - 2.5 grams of adsorbent spiked with a known amount of analyte is placed into a cellulose thimble , which is then placed into the soxhlet extractor. The unit is then placed in the water bath until the bottom portion has been warmed to ca. 20 deg. above ambient, and then the unit is removed from the water bath. The unit is charged with liquid CO_2 as described in the above paragraph. When the pressure rises to ca. 600 psi, the cold water is pumped into the cold finger from the attached ice-bath. The unit is set into the water bath at 2.5 inches and the unit allowed to equilibrate (approx 750 psi).

The cycle proceeds for three hours.At the end of this time, the unit is removed from the water bath, the cold water tubes removed and the unit is placed in an insulated container and cooled with liquid Nitrogen until the pressure drops to zero, at which time the entry valve is 'cracked' and the unit allowed to bleed off the CO_2.

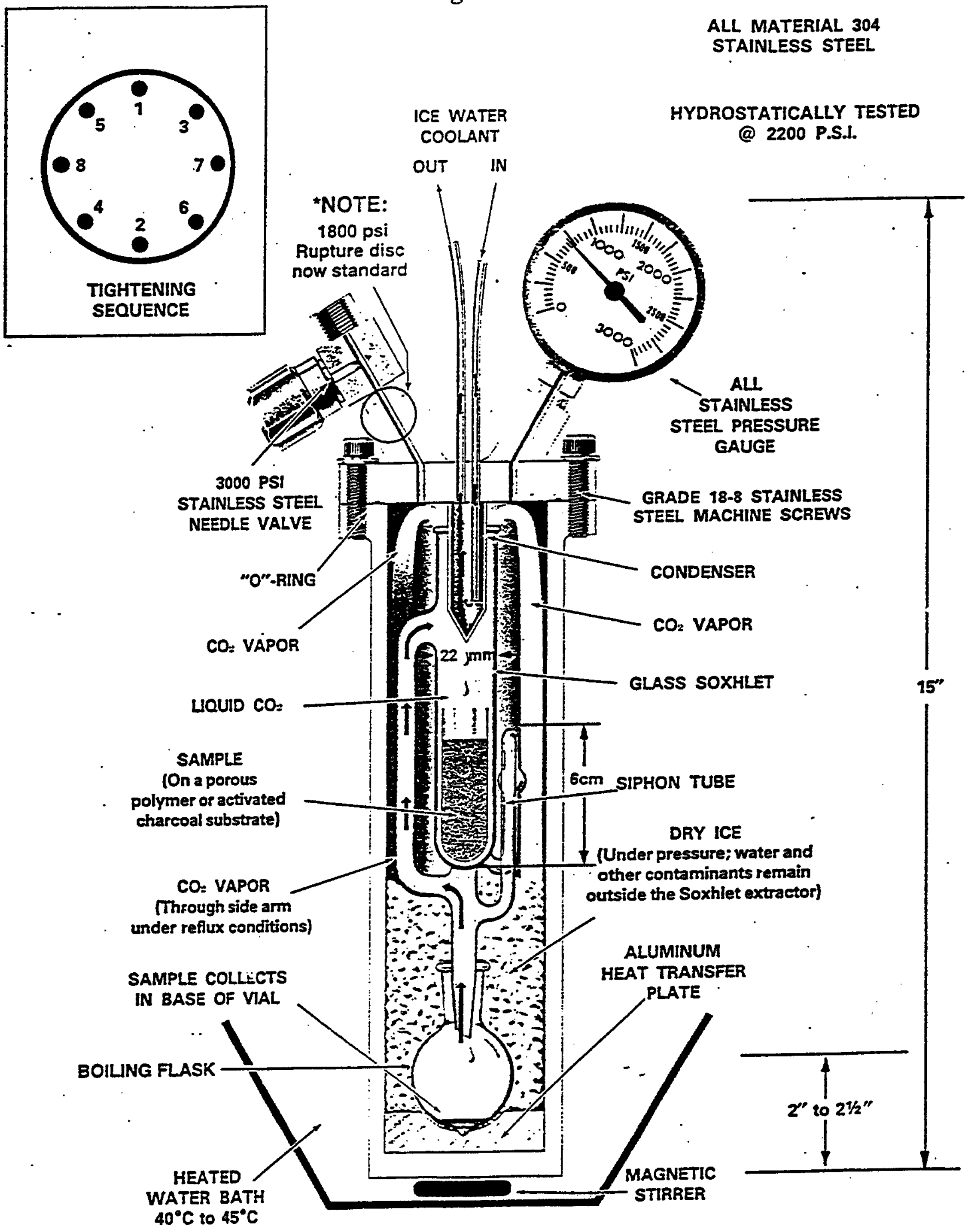
2.3.1 ESTABLISHING CALIBRATION CURVES

Prior to spiking the solid adsorbents, calibration standards of organic compounds that are related to chemical warfare agents were evaluated.The organic compounds chosen were Pinalcolyl Alcohol (PA), Diethyl methylphosphonate(DEMP), Triethyl phosphate (TEPO), Trimethyl phosphate (TMPO), Dimethyl methylphosphonate (DMMP), and Diisopropyl methylphosphonate (DIMP)

A stock solution of 1000 ug/mL of each of the organic phosphonates was made by adding a weighed amount of each to a 10 mL flask and diluting to mark with methylene chloride. Further dilutions were made to obtain 500, 300, 250, 100, 50, and 25 ug/mL. A standard mixture was employed, rather than single components. so as to evaluate the concentrations in a realistic analysis.

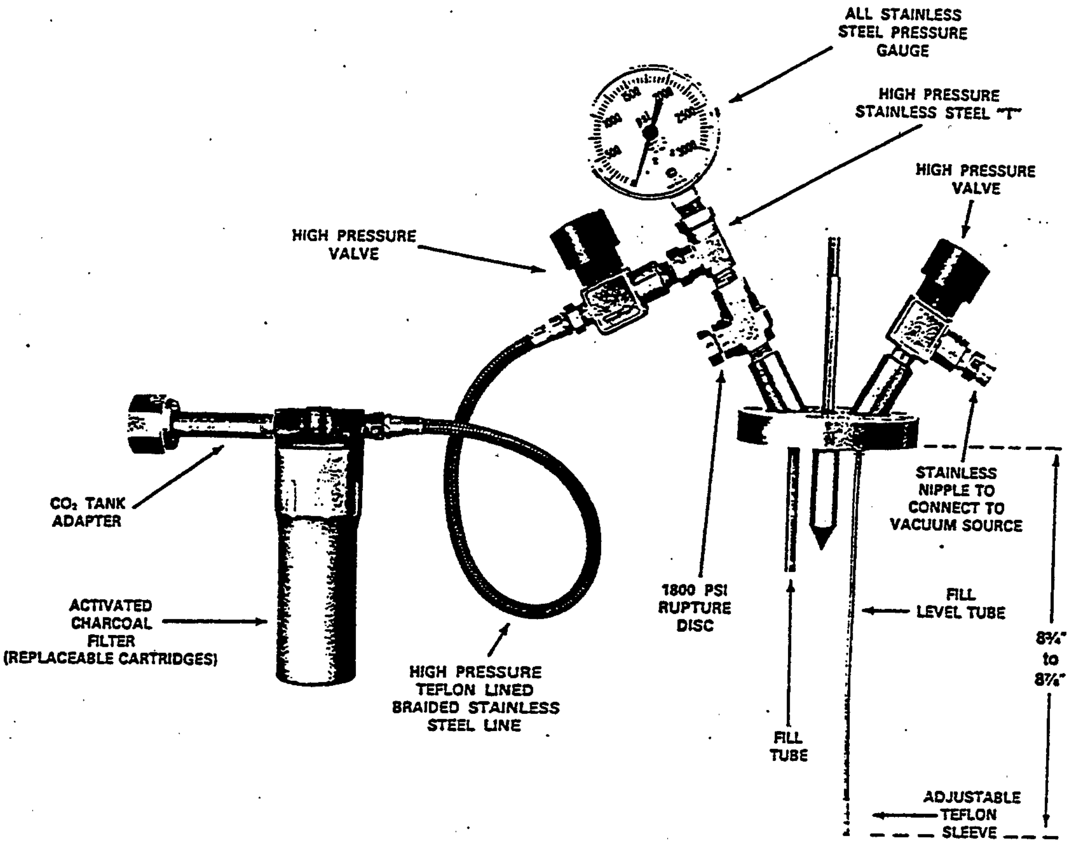
One microliter of each standard mixture was injected into a gas chromatograph interfaced to a liquid Nitrogen cryofocus cooled to a minus 120^0 C. This was ballistically heated to 250^0C, injected into the GC, interfaced to a Mass Spectrometer. Calibration curves were obtained for each concentration and evaluated with respect to area counts.

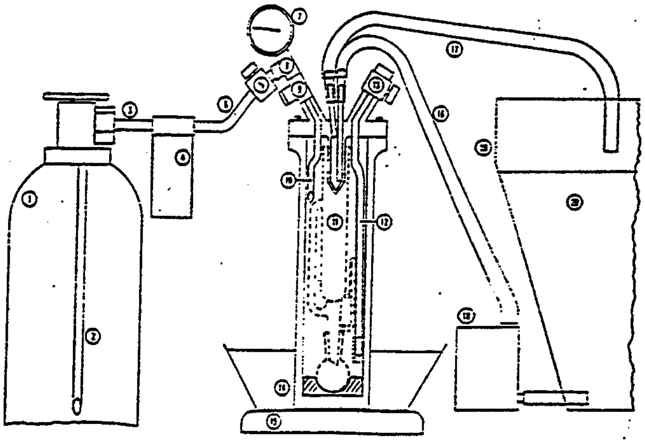
Figure 1



Internal View of Soxhlet Extractor

Figure 2





1. Liquid CO$_2$ Cylinder
2. Dip Tube
*3. CO$_2$ Cyl. Nipple
*4. Activated Charcoal CO$_2$ Purifier
*5. High Pressure Valve No. 1
*6. Teflon Lined H.P. Hose
7. All Stainless Steel Gauge
*8. Street Tee
9. Rupture Disc
*10. Fill Tube
11. Glass Soxhlet Extractor
*12. Outlet Dip Tube With Adjustable Teflon Sleeve
13. High Pressure Valve No. 2
14. Heated Water Bath
15. Hot Plate
16. Flexible Hose
17. Flexible Hose
18. Coolant Pump
19. Ice Chest
20. Water W/Ice

Working Diagram of Soxhlet Extractor

Figures 3, 4, 5, 6, 7 and 8 depict the calibration curves with their respective intercepts, slopes and correlation values.

Figure 3

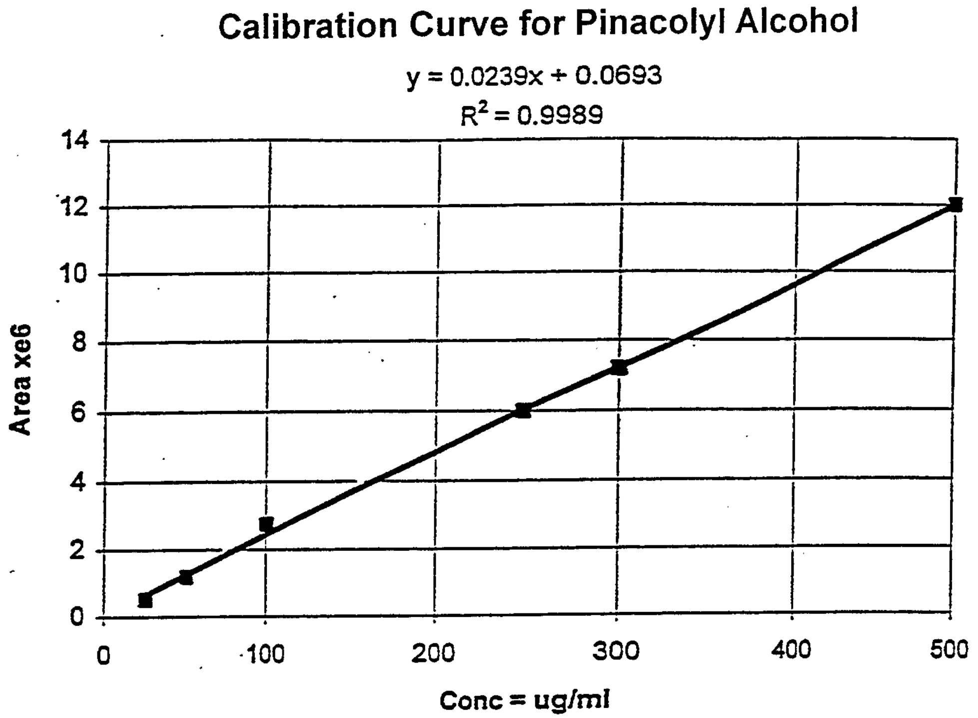


Figure 4

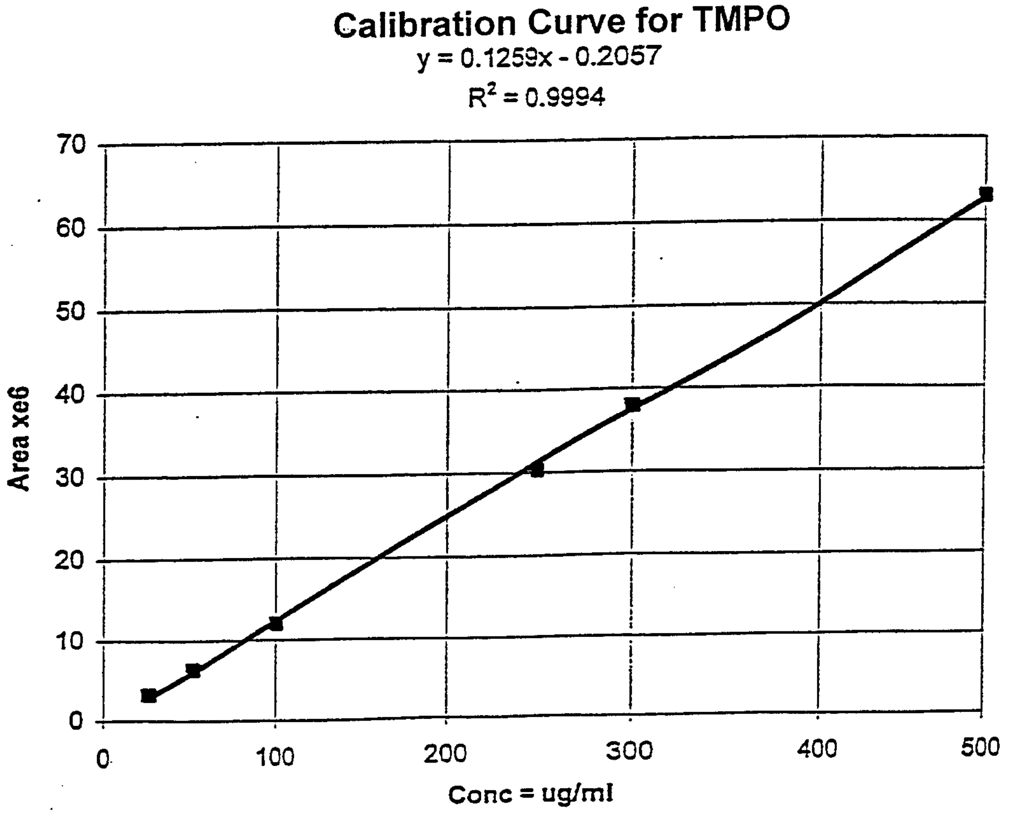


Figure 5.

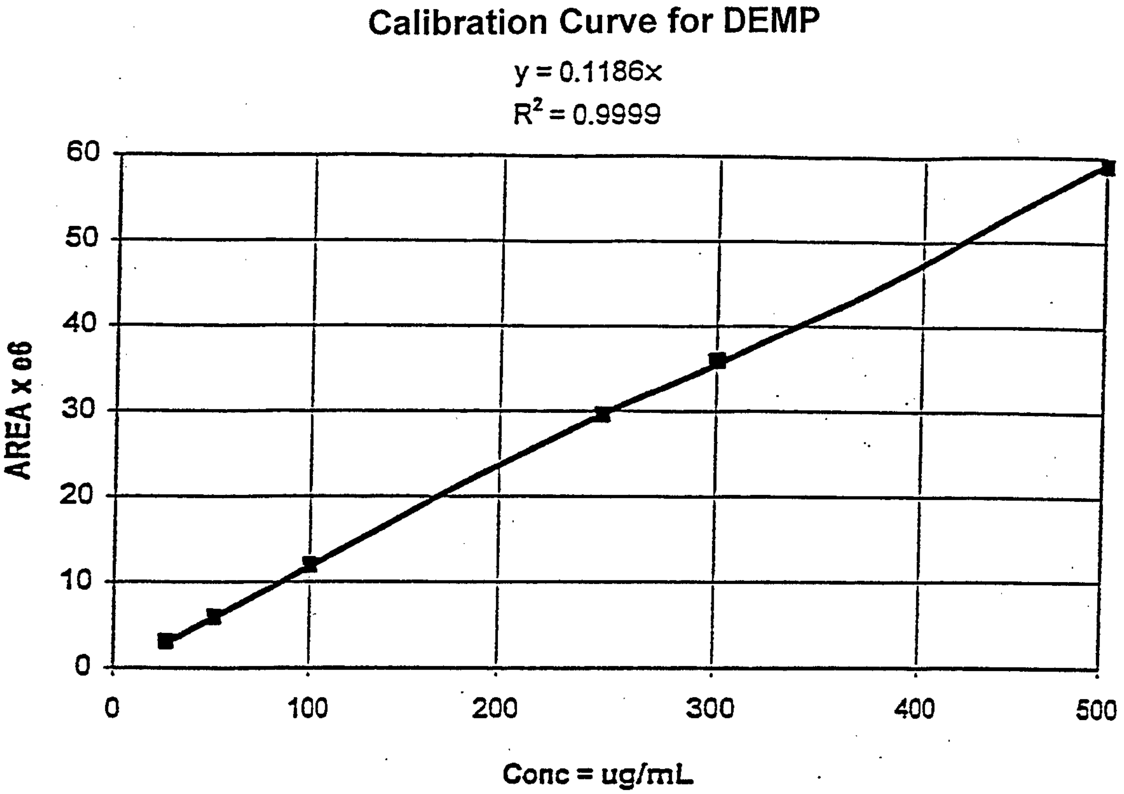


Figure 6

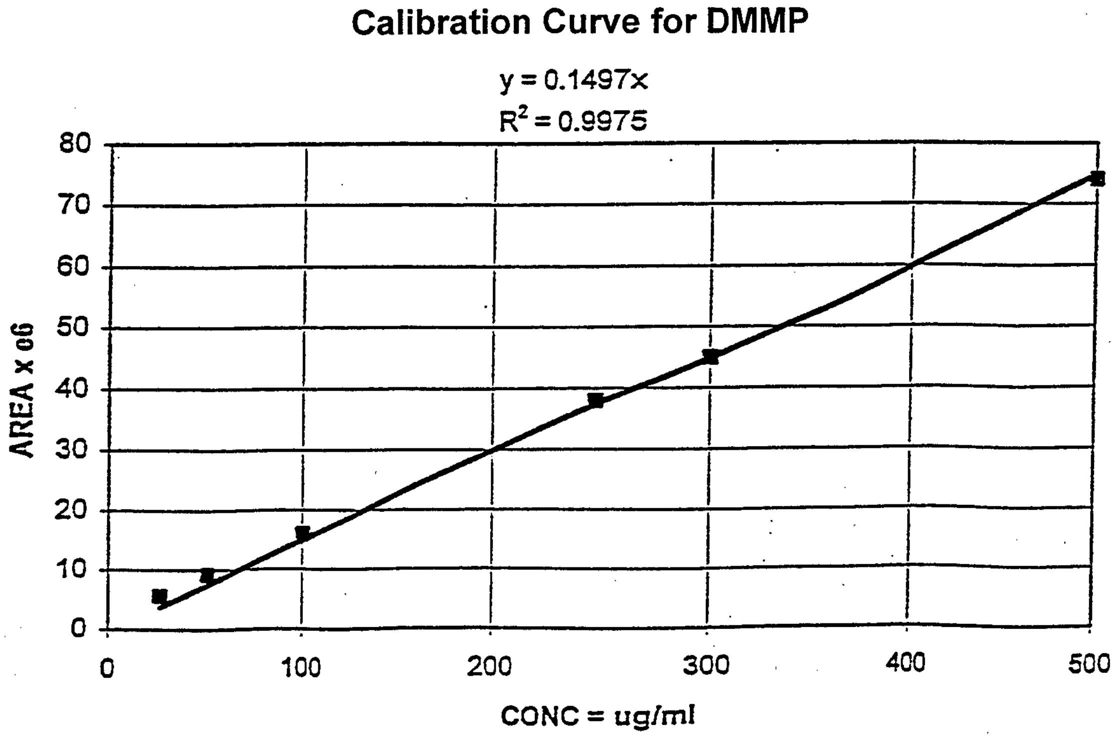


Figure 7

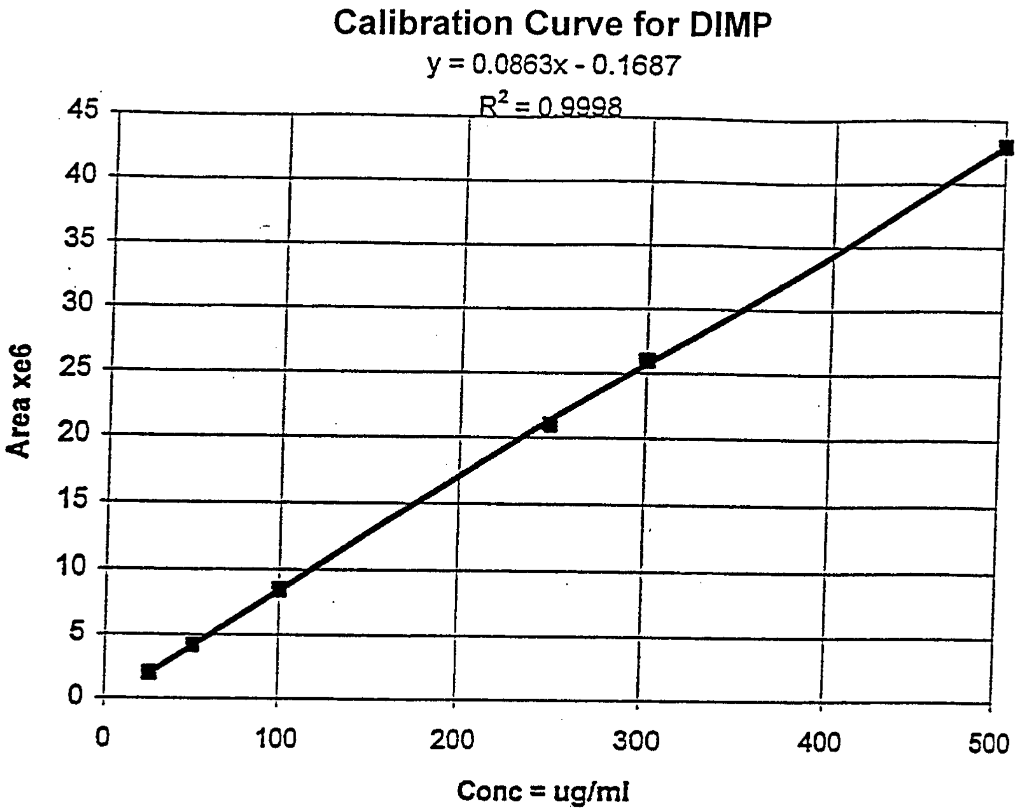
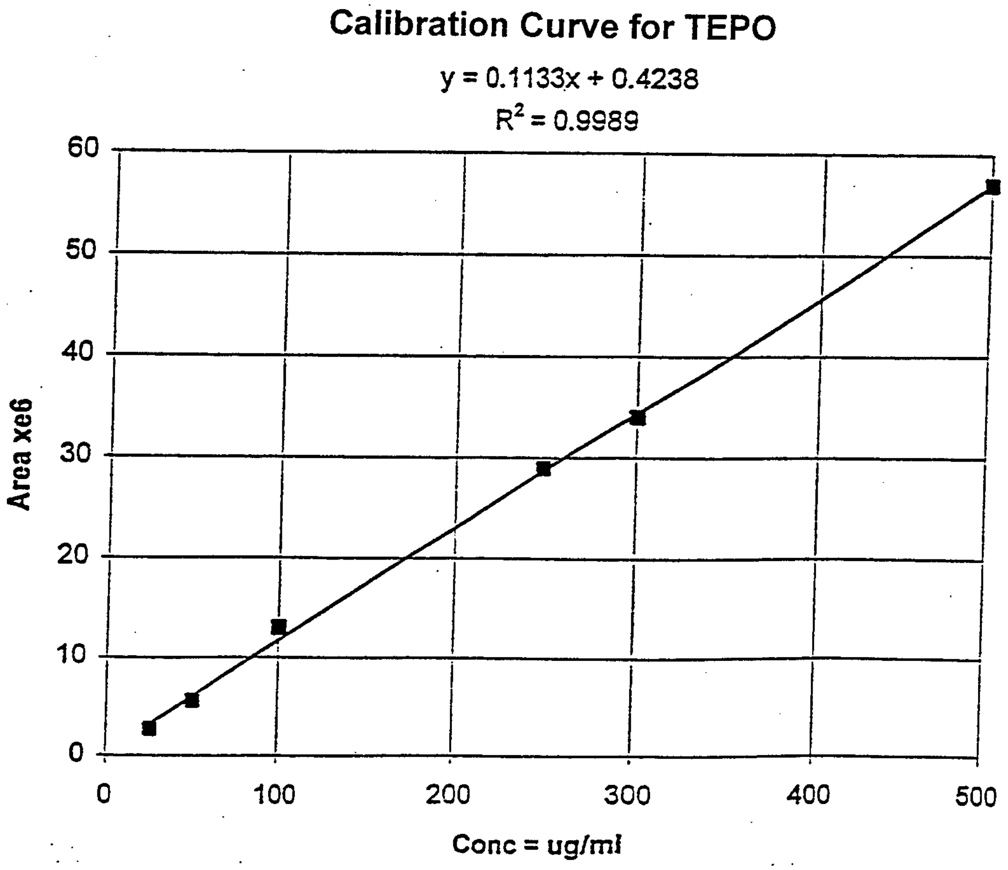


Figure 8



2.3.2 CHROMOSORB 108

One and one-half grams of conditioned Chromsorb 108 (Altech 60/80 mesh) was placed in four separate beakers and each was spiked with 1 mL of 500, 200,100 and 50 ug/mL respectively, of the standard solution in methylene chloride. The contents of each beaker was air dried for one hour at ambient temperature and placed into four cellulose thimbles and extracted for three hours in the High Pressure Extractor at 750 psi, water bath at 50^0 C. and the cold finger at 0^0 C. The condensate was taken up with one milliliter of methylene chloride. 1 uL of the condensate solution was analyzed to determine the concentrations of the extracted analytes. The effective extraction from each of the Chromosorb 108 samples is shown in Table 1.

2.3.3 ACTIVATED CHARCOAL, FISHER C277-350, LOT #904763, 6-12 MESH

Two and one-half grams of the activated charcoal was placed in each of four beakers and spiked with 500, 250, 100 and 25 ug/mL respectively,of the standard solution in methylene chloride. The contents of each beaker was air dried at ambient temperature for one hour and then placed in four cellulose thimbles, extracted with the High Pressure Soxhlet extractor for three hours at 750 psi, water bath at 50^0 C. and the cold finger at 0^0 C. The condensate was taken up with 1 mL of methylene chloride. 1 uL of the condensate solution was used for the analysis. The effective extraction for the activated charcoal is shown in Table 2.

2.3.4 KANSAI SUPERACTIVATED CARBON (MAXSORB, LOT #580A, 50% WATER)

One and one-half grams of the activated charcoal was placed in each of four beakers and the charcoal spiked with 200,100,50 and 25 ug/mL respectively of the standard solution mixture. The spiked samples were air dried for one hour at ambient temperature and then placed in four cellulose thimbles. The samples were extracted in the High Pressure Soxhlet Extractor for three hours at 800 psi, water bath at 50^0 C and the cold finger at 0^0 C. The condensate was taken up with one milliliter of methylene chloride, and 1 uL was used for the analysis.The results for the effective extraction of the Superactivated Carbon are listed in Table 3.

2.3.5 MAXSORB II (ACTIVATED CHARCOAL AS IN SECTION 2.3.4)

One and one-half grams of the activated charcoal was placed in each of two beakers. The contents of one beaker was spiked with 1 mL of the 500 ug/mL standard solution and the contents of the other beaker was spiked with 1 mL of the 250 ug/mL standard solution. The beakers were covered with parafilm and penetrated to leave an opening of 1/8 “ and air dried at ambient temperature for 24 hours. The contents of the beakers were placed into two separate cellulose thimbles and extracted in the High Pressure Soxhlet Extractor for three hours at 750 psi, water bath at 50^0 C. and the cold finger at 0^0 C . The solution was analyzed for the effective extraction under these conditions. The results are listed in Table 4.

Table 1

CHROMOSORB 108

% Recovery

STANDARD	1000 ug/mL	500 ug/mL	200 ug/mL	100 ug/mL	50 ug/mL
PA	45	50	26	30	25
DMMP	60	62	60	60	55
TMPO	62	55	50	48	45
DEMP	78	75	70	65	60
DIMP	83	81	78	75	70
TEPO	83	84	85	83	80

TABLE 2

ACTIVATED CHARCOAL, FISHER C277-0350, LOT #904763

% Recovery

STANDARD	500ug/mL	250 ug/mL	100 ug/mL	50 ug/mL
PA	21	18	20	12
DMMP	27	22	30	26
TMPO	56	25	30	15
DIMP	50	15	18	10
DEMP	52	20	10	8
TEPO	55	25	20	15

Table 3

KANSAI SUPERACTIVATED CARBON

Lot # 508

% Recoveries

STANDARD	200 ug/mL	100 ug/mL	50 ug/mL	25 ug/mL
PA	42	25	30	24
DMMP	46	40	30	33
TMPO	80	75	40	40
DEMP	59	50	45	40
DIMP	73	65	40	35
TEPO	67	78	43	40

Table 4

MAXSORB II (SUPERACTIVATED CARBON)
(24 Hours Partially Covered)

% Recovered

STANDARD	500 ug/mL	250 ug/mL
PA	10	4
DMMP	36	8
TMPO	40	20
DEMP	36	24
DIMP	28	10
TEPO	36	20

2.3.6 MAXSORB III (ACTIVATED CHARCOAL AS IN SECTION 2.3.4)

One and one-half grams of Maxsorb was placed in each of two beakers and the contents spikes with 1 mL of 500 ug/mL and 250 ug/mL respectively, with the standard solution mixture . The beakers were completely exposed to the ambient air for 36 hours. Each of the spiked samples was placed into two cellulose thimbles and extracted in the High Pressure Soxhlet Extractor for three hours at 750 psi,water bath at 50^0C and the cold finger at 0^0 C. The resulting condensate was taken up with 1 mL of methylene chloride and 1 uL of the condensate solution was used for the analysis. The results of the effective extraction under these conditions are listed in Table 5.

2.3.7 CHROMOSORB 108/NOMEX POLYMER

One gram of Chromosorb 108 / Nomex Polymer was placed in a beaker and spiked with 0.5 mL of the 1000 ug/mL standard solution mixture in methylene chloride, air dried at ambient temperature for one hour. The spiked sample was placed in a cellulose thimble and extracted in the High Pressure Soxhlet extractor for three hours at 750 psi, water bath at 50^0 C. and the cold finger at 0^0 deg C. The resultant condensate was taken up with 0.5 mL of methylene chloride and 1 uL of the condensate solution was analyzed for the effective extraction . The results are shown in Table 6.

2.3.8 TENAX GC/NOMEX POLYMER 3:1 RATIO #6669-30 22.3% SOLIDS

One gram of the mixture of Tenax GC and the Nomex Polymer was placed in a beaker and the adsorbent spiked with 0.5 mL of the 1000 ug/mL standard solution mixture.The sample was exposed to the ambient air for 24 hours and then placed into a cellulose thimble, extracted in the High Pressure Soxhlet Extractor for three hours at 750 psi, water bath at 50^0 C. and the cold finger at 0^0 C. The resultant condensate was taken up with 0.5 mL of methylene chloride and 1 uL of the condensate solution used for the analysis. The percent recovery for each analyte is listed in Table 7.

2.3.9 ANDERSON CARBON/NOMEX POLYMER 3:1 RATIO #1041-46

One and one-half grams of the Anderson Carbon / Nomex Polymer was placed in a beaker and the adsorbent was spiked with 0.5 mL of the 1000 ug/mL of the standard solution mixture. The spiked sample was exposed to the ambient air for 24 hours and then placed into a cellulose thimble and extracted in the High Pressure Soxhlet Extractor for three hours at 750 psi, water bath at 50^0 C. and the cold finger at 0^0 C. The resultant condensate was taken up with 0.5 mL of methylene chloride and 1 uL of the condensate solution was used for the analysis. The percent recovery for each analyte is listed in Table 8.

Table 5

MAXSORB III (SUPERACTIVATED CARBON)
(36 Hours at Ambient Temperature)

% Recovery

STANDARD	500 ug/mL
PA	BDL*
DMMP	BDL *
TMPO	10
DEMP	BDL*
DIMP	BDL*
TEPO	BDL*

*Below detection level.

Table 6

CHROMOSORB 108/NOMEX POLYMER
(0.5 mL of 1000 ug/mL of standard mixture)

STANDARD	% Recovered
PA	BDL*
DMMP	50
TMPO	61
DEMP	63
DIMP	65
TEPO	67

*Below detection level

Table 7

TENAX GC/NOMEX POLYMER

(3:1 Ratio #6669-30 2.3% Solids)

(0.5 mL of 1000 ug/mL + 0.5 mL CH_3OH)

STANDARD	% Recovered
PA	BDL*
DMMP	47
TMPO	45
DEMP	24
DIMP	13
TEPO	10

*Below detection level

Table 8

ANDERSON CARBON/ NOMEX POLYMER

(3:1 Ratio #1041-46)

(0.5 mL of 1000 ug/mL of Standard Mixture)

STANDARD	% Recovered
PA	BDL*
DMMP	2
TMPO	2.5
DEMP	1.0
DIMP	1.0
TEPO	1.0

*Below detection level

3. CONCLUSION

3.1 DISCUSSION

This study has demonstrated the effectiveness of the extraction of organic phosphonates from various adsorbents. Chromosorb 108 appears to be the most effectively desorbed for the concentrations of the phosphonates used in this study. However, it is demonstrated that charcoal can also be desorbed but not as effectively as Chromosorb 108. The efficiency of desorption is dependent upon the amount of phosphonate initially present and the exposure of the adsorbent to the atmosphere. However, the study does indicate that if the adsorbent is enclosed soon after it is exposed, the phosphonates could be detected. Knowing the amount extracted from the analysis, and the effectiveness of desorption from this study, the initial amount present can be predicated.

3.2 EXTRACTION EFFICIENCY

Parameters affecting the extraction speed and the effectiveness of extraction in this study are:

Weight of CO_2 added:	150 - 200 g
Temperature of cold finger:	0 deg C.
Temperature of water bath:	50 - 51 deg C.
Height of immersion in water bath:	2.5 inches
Resultant vessel pressure	750 - 800 psi

These conditions result in a cycle rate of approximately 20 cycles per hour (600 mL of CO_2 /hr. or 30 mL of CO_2 every three minutes)[1] Each run was 3.5 - 4.0 hours, representing approximately 2.0 - 2.5 liters of solvent passing through the sample.

4. FUTURE RESEARCH

Initially, the High Pressure Soxhlet Extractor was used in this laboratory to desorb organic phosphonates from a commercial product called SAKRETE. The effectiveness of desorption was extremely poor or below detection level, probably due to the high pH of the product. Further studies could focus on the desorption of organic phosphonates from various types of matrices, and from solid material that can be placed in the cellulose thimble.

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LITERATURE CITED

1. Rood, Dean; Dinnauer, Marc; Soholsky,Kevin; Unpublished report as Supplementary Instructions for filling the Pressurized Soxhlet Extractor (1993). J & W Scientific Co.,91 Blue Ravine Rd., Folsom, CA.

2. Figee, K.; Rahel, W.; Wicer, A.; Frezenius Z. Anal Chem (1987), 327, pp 261 - 278. Adsorbents for the Enrichment of Organic Atmospheric Trace Compounds.

3. Fowler, William K. and Miller, Herbert C., Study of Solid Sorbents for GB and Mustrard Dosimeters (September 1977 - November 1979) Contract # DAAK11-0086, Southern Research Institute, Birmingham,AL April 1980 (AD B047 706L)

4. Ellzy, Michael W.; Pleva, Stephen G., Collection of Chemical Warfare Related Compounds On Solid Adsorbents , EDRDEC -TR- 050, Research and Technology Directorate, July 1993.