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High Capacity Anion-Exchange Resin as a Solid-Phase Extraction for Determination of Methylphosphonic Acid

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A highly sensitive and accurate method for the preconcentration and determination of ultratrace amounts of methylphosphonic acid (MPA) in water samples is proposed. The method is based on the solid phase extraction with an ion exchange anion resin. The high capacity anion-exchange was prepared from the reaction of polyvinylbenzyl chloride and 2,3,4-tris((dimethyl amino)methyl)phenol in dioxane. The ion-exchange capacity was estimated by the potentiometric titrations and calculated as 8.6 meq/g-dry. The extraction efficiency and the influence of the type and least amount of eluent for the stripping of MPA from the cartridge, pH, flow rates of sample solution and eluent, resin stability and reproducibility, and the breakthrough volume were evaluated. The limit of detection of the method was 0.5 μg L^{-1} for MPA and also an enrichment factor of 100 was obtained.

Keywords ion-exchange; nerve agent; polyvinylbenzyl chloride; solid phase extraction; 2,3,4-tris((dimethyl amino)-methyl)phenol

INTRODUCTION

The Chemical Weapons Convention (CWC), which came into force in April 1997, forbids the development, production, stockpiling, or use of chemical weapons (CW) (1). Among Chemical Warfare Agents (CWA), nerve agents are known to be highly toxic and powerful inhibitors of acetylcholinesterase. When the nerve agent of the G series, isopropyl methylphosphofluoridate (sarin, GB), pinacolylmethylphosphofluoridate (soman, GD), cyclohexyl methylphosphonofluoridate (cyclosarin, GF), S-2-diisopropylaminoethyl O-ethyl methylphosphonothiolate (VX), and *O*-isobutyl *S*-(2-diethylaminoethyl)methyl phosphothioate (RVX) are exposed to the environment, they are rapidly hydrolyzed to the corresponding alkyl methylphosphonic acids and finally converted to methylphosphonic acid (MPA) (2,3). The degradation pathways of nerve agents are outlined in Fig. 1. The nonvolatile and highly polar methylphosphonic acid is a poor UV absorber. Moreover, since it is readily soluble in water, its presence can be expected in soil and water of regions contaminated with nerve agents. In order to measure the ultratrace level of MPA in water, an analytical method with low limit of detection (LOD) level is required.

Interest in the ultratrace-level detection of the alkylphosphonic acids has increased sharply in the last few years in response to monitoring efforts needed for anti-terrorist activities and to those defined by the Chemical Weapons Convention. State-of-the-art analytical procedures were employed to demonstrate the deployment of chemical agents during the Iraq-Iran conflict (4). Several analytical methods have been reported for analysis of MPA, such as gas chromatography (GC) (5–7), high-performance liquid chromatography (HPLC) (7–9), capillary electrophoresis (CE) (11,12), and ion chromatography (IC) (13,14). Present analytical and separation methods practically resolve all kinds of analytes with detection limits down to the nanogram range. However, their sensitivity and selectivity are usually insufficient for direct determination of the target compound at a very low concentration level in complex matrix samples. Therefore, a sample pretreatment step prior to analysis is usually necessary. Surveys show that more than 80% of analysis time is spent on sample collection and sample preparation. The whole analytical process can be wasted if an unsuitable sample preparation method has been employed before the sample reaches the analyzer (15,16). Solid-phase extraction (SPE) has been widely used for its high selectivity and good reproducibility (17–18). Ultratrace detection of the alkylphosphonic acids presents unique challenges for the analytical chemists. Indeed, relevant contaminants are usually present at low concentration levels and mixed with a large amount of interferences. Therefore, the detection of the target analytes requires analyte preconcentration and elimination of the coeluting interferences that can affect the reliability and sensitivity of the whole analytical procedure. SPE has been successfully used for extraction of AMPAs and MPA from soil and urine samples (19,20). Sega et al. (5) developed a procedure using SPE on amine ion-exchange columns. A SPE column was

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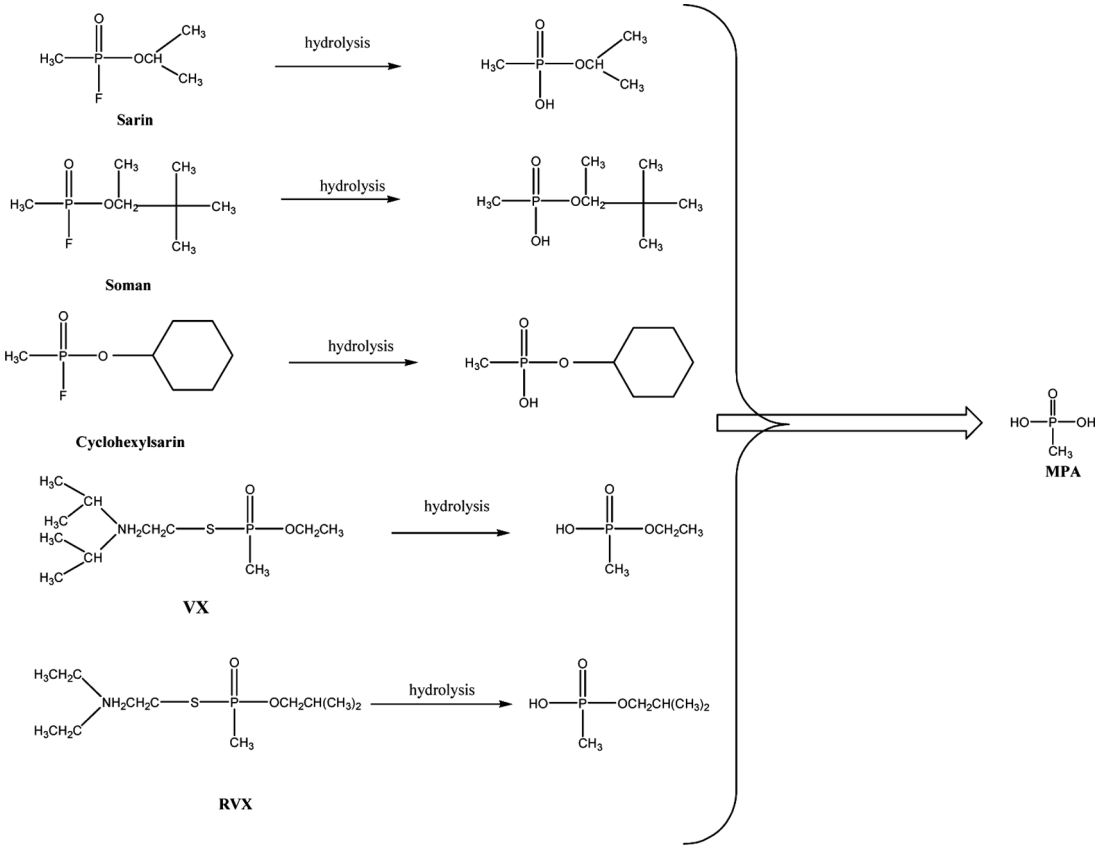

FIG. 1. Degradation pathways of nerve agents.

packed with silica with a bonded quaternary amine phase. LOD of 3.4 $\mu g\,L^{-1}$ were achieved for MPA in pure water. Wang et al. (21) investigated the extraction efficiencies of four cartridges, ODS-C_{18}, C2, CN, and SAX, for MPA in water samples. The results have shown that the recoveries of MPA were higher with SAX than the other cartridge and LOD of 6 $\mu g\,L^{-1}$ were achieved in human plasma. In this paper, we developed a method of direct extraction of MPA from water with a novel anion-exchange resin as a solid-phase extraction (SPE) sorbent with increased resin exchange capacity and to lower the LOD.

EXPERIMENTAL

Reagents

MPA, Polyvinylbenzyl chloride ($M_w = 100000$) and 2,4,6-Tris(dimethylaminomethyl) phenol were purchased from the Aldrich Chemical Co. The derivatization reagent bis(trimethylsilyl) trifluoroacetamide (BSFTA) was obtained from ACROS. The following chemicals were from Merck and of the highest purity: sodium nitrate, potassium chloride, silver nitrate, ammonia, acetic acid, nitric acid, hydrochloric acid, and analytical grade methanol and dioxane. Doubly-distilled deionized water was used throughout. Stock solutions (1000 mg L^{-1}) were prepared by dissolving the appropriate amounts of MPA in water. All working solutions were prepared by diluting stock solutions to appropriate concentration with double-distilled water.

Instrumentation and Analytical Conditions

Elemental analysis was carried out by Heraeus CHN-O-Rapid elemental analyzer. A Varian Model 3400 capillary GC system was used for all measurements. The temperature of the injector and the detector was 240°C. The column oven temperature was set initially at 70°C (2 min hold) and then programmed at 20°C/min to 180°C, thereafter at 30°C/min to 240°C (4 min hold). Nitrogen was used as carrier gas and the FID temperature was set at 250°C. The pH was determined with a model 691 Metrohm pH meter with a combined glass-calomel electrode. The analyte solutions were adjusted by adding an appropriate amounts of 0.1 M either HCl or ammonia solutions to a fixed pH.

Synthesis of High Capacity Anion-Exchange Resin

To a solution of polyvinylbenzyl chloride (PVBC) (1.0 g, 5.5 mmol) in dioxane (25 mL), 2,3,4-tris((dimethyl amino)-methyl)phenol (22 mmol) was added and stirred for 12 h

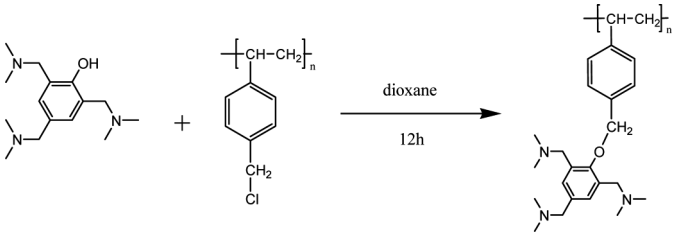

FIG. 2. The synthetic pathway for anion-exchange resin.

at room temperature. The product precipitates as graft proceeds (Fig. 2). The solvent was evaporated off under vacuum and the crude polymer was washed with water and finally with methanol, and was dried in an oven maintained at 70–75°C. The solubility behavior of the resin was qualitatively tested in some of the typical organic solvents. The resin was insoluble in acetone, acetonitrile, chloroform, toluene, and aprotic solvents such as NMP, DMF, and DMSO.

Determination of Ion-Exchange Capacity (IEC) of Resin

0.5 g of Ion-exchanger was immersed with 20 mL of 2 mol/L KCl and HCl for 12 h in order to convert the counter ion to the Cl^- form and then sufficiently washed with deionized water. Thereafter, the ion-exchanger was immersed in 20 mL of 2 mol/L $NaNO_3$ and stirred for 1 h. This treatment was repeated four times in order to elute Cl^- from the membrane thoroughly and all eluents were collected. The collected solutions were titrated with 0.1 mol/L $AgNO_3$ (22). IEC of 8.6 meq/g-dry is calculated.

Procedure of Extraction, Elution, and Determination of MPA

The packed SPE columns were prepared by packing 0.2 g of resin into the cartridge. The cartridge was clean and the condition was by passing 5 mL of methanol, which removes all contaminants arising from the manufacturing process and the environment. After drying the cartridge, a solution of 0.5 μg MPA from a 50 mL sample was introduced onto the cartridge and allowed to penetrate inside the cartridge completely. The extracted ions were stripped from the cartridge using 2 mL solution of Methanol: Ammonia (80:20 v/v) at 1 mL min^{-1} flow rate. The eluted solution was concentrated and dried at 50°C and then BSFTA and pentane were added. The mixture was heated at 40°C for 15 min (23) and the BSFTA derivative of MPA obtained was analyzed by GC.

RESULT AND DISCUSSION

Synthesis and Estimation of Amination Degree of Resin

The reaction between PVBC and 2,3,4-tris((dimethyl amino)methyl)phenol in dioxane leads to the formation of resin as pale yellow solid. The determination of the amination degree of PVBC in terms of amination percent, elemental analysis was first performed. The percentages of 66.55, 6.05, and 8.35 were obtained for C, N, and H elements, respectively. The carbon-to-nitrogen weight% ratio was obtained to be 11.00. Then, the carbon-to-nitrogen ratios for different theoretically aminated PVBC with different amination degree were calculated. A plot of calculated C/N% versus PVBC amination% has been shown is Fig. 3. As indicated, an 11% for C/N weight ratio corresponds to 30% amination of PVBC. This indicates that one-third of all potentially exchangeable sites, in terms of functional group transformation, in the PVBC resin, have been successfully aminated.

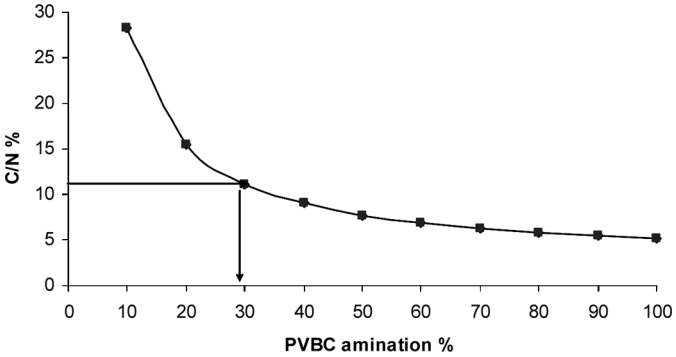

FIG. 3. C/N % as a function of PVBC amination %.

SPE Optimization

Choice of Eluent

In order to choose the most effective eluent for quantitative stripping of the retained ions after extraction of 0.5 μg MPA form 50 mL sample, the MPA ions were stripped with 1–5 ml of different effluent. The resulting data are listed in Table 1. From the data given in Table 1,

TABLE 1
Percent recovery of MPA from the cartridge using 2 mL of different stripping solution

Stripping solution	Recovery mean (%) ± SD[a]
HNO_3 (0.1 M)	20 ± 3
HCl (0.1 M)	21 ± 2
CH_3COOH (0.1 M)	32 ± 1
Methanol:Ammonia (95:5)	80 ± 6
Methanol:Ammonia (90:10)	91 ± 4
Methanol:Ammonia (80:20)	99 ± 5
Methanol:Ammonia (60:40)	95 ± 5
Methanol:Ammonia (50:50)	93 ± 2

[a]SD, standard derivation for n = 3.

it is immediately obvious that among the different solutions, 2 mL of Methanol:Ammonia (80:20 v/v) can accomplish the quantitative elution of MPA from the cartridge, while the other solutions are ineffective for the complete elution of MPA. With 2 mL of the effluent the recovery was 99% and in all experiments, this volume of the stripping solution was used. The influence of percentage Methanol:Ammonia on the stripping efficiency is also included in Table 1. Under acidic condition MPA is fully protoned but, derivatization cannot be successfully performed on this species, and therefore the intensity of the corresponding peak in GC is reduced. In other words, although under acidic condition the MPA ions disrupt the resin, but they cannot be detected by GC. Also, it has to be noticed that the MPA salt produced under basic condition is needed to be soluble in BSFTA for successful derivatization. This is suitable for ammonium salt, but not for sodium and potassium salts (23,24). Practically, when the sodium or potassium salts were employed, a greatly reduced peak area was obtained for equivalent amounts of ammonium salts. It was visually obvious that the sodium or potassium salts were not completely dissolved. Ammonium salt was completely soluble in the pure reagent, BSFTA.

Effect of pH on the Adsorption of MPA Ions

The pH of the sample solution is one of the influencing factors in the solid phase extraction process. The analyte solutions were adjusted by the addition of appropriate amounts of 0.1 M either HCl or ammonia solutions to a fixed pH and passed through a cartridge. The pH range studied was between 3.0 and 10.0. It was found that the percentage recovery is nearly independent of pH at pH 4–7. Figure 4 illustrates the effect of the sample pH on MPA retention showing the recovery obtained using different sample pH. pKa values of MPA and monoalkyl ester have been reported to be 2–3 (25) and MPA exist as deprotonated forms in the pH > 3. Under neutral pH and weakly acidic condition MPA exist as a strong anion and therefore are efficiently trapped on the resin.

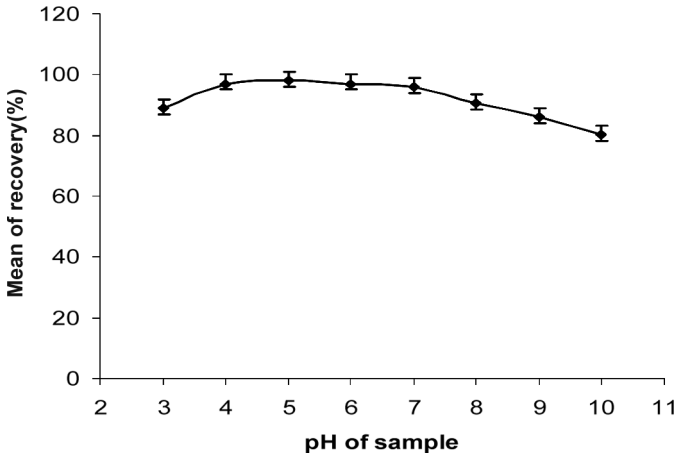

FIG. 4. Percent recovery of MPA in 3–10 pH range.

Effect of Sample Flow-Rate and Breakthrough Volume

The dependency of the uptake of the MPA on the flow rate was studied. The flow rate of the solution through the cartridge varied from 1 to 5 mL min^{-1}. Adsorption of MPA was quantitative and reproducible in this range and not considerably affected by the sample solution flow rate. Thus, the flow rate of the sample solution was maintained at 5 mL min^{-1} throughout the experiment. Quantitative stripping of MPA from the cartridge achieved in a flow rate range of 0.5–4 mL min^{-1}, using two times 2 mL of Methanol:Ammonia (80:20 v/v) as a stripping solution. At higher flow rates, a large volume of eluent was necessary for the quantitative stripping of ions. Hence, subsequent experiments were carried out with a flow rate of 1 mL min^{-1}.

The measurement of the breakthrough volume is important in SPE because the breakthrough volume represents the sample volume that can be preconcentrated without loss of analyte during elution of the sample. The breakthrough volume of the sample solution was tested by dissolving 0.5 μg of MPA in 50, 100, and 200 mL in water and the recommended procedure was followed. In all cases, the extraction was found to be nearly quantitative. Thus the breakthrough volume for the method should be greater than 200 mL. Consequently, by considering the final elution volume of 2 mL and the sample solution volume of 200 mL, an enrichment factor of 100 was easily achievable.

Method Validation

To test the resin stability and reproducibility, it was subjected to several loading and elution batch operations. The operating capacity was calculated from the loading and elution tests. The results from both tests agreed within 1–3% error up to 20 cycles of repeated experiments.

Calibration graphs obeyed the equation $A = 3.01 \times 10^{-1} C + 3.52 \times 10^{-2}$ ($r^2 = 0.998$), where A is the integrated area and C is the MPA concentration in μg L^{-1}. The linear calibration curve was within the concentration range from 1.3 to 250 μg L^{-1}. The detection limit (3σ) and the quantification limit (10σ), defined as by IUPAC (26,27) were found to be 0.5 and 1.3 μg L^{-1} for 50 mL samples, respectively, The relative standard deviation of the 10 replicate determinations was 2.4% for the determination of 0.5 μg of MPA in 50 mL water sample.

CONCLUSION

A new anion exchange resin was prepared from a substitution reaction between polyvinylbenzyl chloride and 2,4,6-Tris (dimethylaminomethyl) phenol. Since every individual Cl functional group in the starting polymer is replaced with a new group involving three $-N(Me)_2$

functional groups, high IEC can be prepared. Accordingly, the capacity of the current resin reached 8.6 meq/g-dry. This is to be compared with the commercial chloride form of the strong base IEC, which has the exchange capacity of 1.86 meq/g of wet resin with 43.35% moisture (or capacity of 2.97 meq/g of dry resin). Considering the fact that a charged cartridge with the resulting resin has an enrichment factor 100 for MPA and its limit of detection is $0.5\,\mu g\,L^{-1}$, we expect this resin has to be used for the separation of trace level of other anions. SPE with high capacity anion-exchange resin is an efficient methodology for the preconcentration and separation of trace MPA in aqueous solutions. Results presented in this work demonstrate the possibilities offered by the capacity anion-exchange resin as a sample preparation method for trace analysis amounts of MPA in water samples. This method is a precise and accurate alternative to conventional procedures for determining the trace MPA in water samples.

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