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Nanoporous Organosilicas as Preconcentration Materials for the Electrochemical Detection of Trinitrotoluene

Scott A. Trammell,[†] Mazyar Zeinali,[‡] Brian J. Melde,[†] Paul T. Charles,[†] Freddie L. Velez,[§] Michael A. Dinderman,[†] Anne Kusterbeck,[†] and Michael A. Markowitz^{*,†}

Center for Bio/Molecular Science and Engineering, Code 6900 Naval Research Laboratory, Washington, DC 20375, nEnvironmental, LLC, P.O. Box 1126, Columbia, Maryland 21044, and University of Maryland Eastern Shore, Princess Anne, Maryland 21853

We describe the use of nanoporous organosilicas for rapid preconcentration and extraction of trinitrotoluene (TNT) for electrochemical analysis and demonstrate the effect of template-directed molecular imprinting on TNT adsorption. The relative effects of the benzene (BENZ)- and diethylbenzene (DEB)-bridged organic–inorganic polymers, having narrow or broad pore size distributions, respectively, on electrochemical response and desorption behavior were examined. Sample volumes of 0.5–10 mL containing 5–1000 ppb TNT in a phosphate-buffered saline buffer were preconcentrated in-line before the detector using a microcolumn containing 10 mg of imprinted BENZ or DEB. Square-wave voltammetry was used to detect the first reduction peak of TNT in an electrochemical flow cell using a carbon working electrode and a Ag/AgCl reference electrode. Imprinted BENZ released TNT faster than imprinted DEB with considerably less peak tailing and displayed enhanced sensitivity and an improvement in the limit of detection (LOD) owing to more rapid elution of TNT from that material with increasing signal amplitude. For imprinted BENZ, the slope of signal versus concentration scaled linearly with increasing preconcentration volume, and for preconcentrating 10 mL of sample, the LOD for TNT was estimated to be 5 ppb. Template-directed molecularly imprinted DEB (TDMI-DEB) was 7-fold more efficient in adsorption of TNT from aqueous contaminated soil extract than nonimprinted DEB.

A major obstacle for field analytical techniques is obtaining a sufficient quantity of a compound at concentrations that can be measured by existing instrumentation. More efficient sample collection strategies would decrease the analysis time and improve the detection limits for a wide range of methods, including ion mobility spectroscopy (IMS), biosensors, or surface acoustic wave (SAW) devices. For homeland security and military needs in particular, rapid detection of trace levels of explosives would

provide significant benefits. We have implemented studies to use nanoporous organosilicas imprinted for nitroaromatics, including the explosive trinitrotoluene (TNT), for rapid in-line preconcentration and extraction with highly sensitive electrochemical techniques. This preconcentration allows the collection of enough quantity of the analyte to obtain a detectable signal when only trace amounts of analyte are present in a sample.

Solid-phase extraction (SPE) techniques have been successfully applied to the preconcentration of aromatic explosives.^{1,2} Commercially available resins such as divinylbenzene–vinylpyrrolidone (Porapak R) and divinylbenzene–ethylvinylbenzene (LiChrolute EN) have been tested using microscale SPE for determination of nitroaromatics in aqueous samples and show promise in significantly lowering limits of detection (LODs).³ However, both the breakthrough thresholds and recovery percentages reported have been poor. In addition, the numerous steps involved in SPE can be time-consuming.⁴ As such, developing techniques and new materials specifically for rapid detection when deployed in the field are areas of research still worth pursuing.⁵

To achieve the goal of efficient preconcentration, the preconcentrator must have the following attributes: selectivity, high adsorption capacity, rapid adsorption/desorption kinetics, and low fouling. Because of their high adsorption capacity⁶ as well as mechanical and thermal stability,^{7,8} organosilica sorbents synthesized via surfactant templating^{9–11} are gaining increasing attention

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* To whom correspondence should be addressed. E-mail: Michael.Markowitz@nrl.navy.mil.

[†] Naval Research Laboratory.

[‡] nEnvironmental, LLC.

[§] University of Maryland Eastern Shore.

as preconcentrating materials.¹² Mesoporous polysilsesquioxane organosilicas synthesized via surfactant templating have alternating siloxane and organic moieties that give these materials structural rigidity and a degree of hydrophilicity useful for applications in aqueous systems, with improved accessibility to functional sites due to their open pore structure.^{13–21}

Depending on the rigidity of the bistrialkoxysilane precursor, the resulting material may have narrow or broad pore size distributions.⁶ Surfactant templating is known to yield benzene-bridged polysilsesquioxanes with highly ordered pore structures and very narrow pore size distributions, whereas similarly prepared diethylbenzene-bridged polysilsesquioxanes have random pore structures with broad pore size distributions although much higher adsorption capacity for liquid phase extraction of aromatic compounds.^{22,23} In this paper, by using square-wave voltammetry with molecularly imprinted benzene- and diethylbenzene-bridged mesoporous organosilica preconcentration materials in-line before a glassy carbon electrode, we demonstrate significant enhancement in detection limits using an electrochemical flow cell. The preconcentration materials were molecularly imprinted for TNT using decylaminetrinitrobenzene via template-directed molecular imprinting^{24–29} during synthesis of the benzene (BENZ)- and diethylbenzene (DEB)-bridged hybrid organic–inorganic polymers. Since an effective preconcentration sorbent must effectively adsorb analytes and then release them on demand, the relative effects of the BENZ- and DEB-bridged organic–inorganic polymers, having narrow or broad pore size distributions, respectively, on electrochemical response and desorption behavior were examined. Also, the effect of template-directed molecular imprinting on TNT adsorption from aqueous contaminated soil extract was investigated.

EXPERIMENTAL SECTION

Materials. The organosilica precursors, 1,4-bis(triethoxysilyl)benzene (95%) and bis(trimethoxysilyl)benzene (95%, mixed

meta and para isomers), were purchased from Gelest, Inc. (Tullytown, PA) and stored in a N₂ atmosphere prior to use. Brij76, NaOH, HCl, ethanol, *p*-cresol, *p*-nitrophenol, decylamine, and diethyl ether were purchased from Sigma-Aldrich (St. Louis, MO). Phosphate-buffered saline (PBS) was obtained from Pierce Biotechnology. The PBS buffer contained 0.1 M sodium phosphate and 0.15 M NaCl at pH 7.2. The column, tubing, and low-pressure fittings were from Bio-Rad Laboratories. Analytical stock samples of TNT (1000 µg/mL solution in acetonitrile) were obtained from Radian International. Acetonitrile was obtained from Aldrich and used as received. Deionized water (18 MΩ) was obtained from a Milli-Q water purification system (Millipore).

Preparation of Mesoporous Organosilicas. Imprinted and nonimprinted BENZ-bridged and DEB-bridged polysilsesquioxane mesoporous organosilicas were prepared using Brij76 surfactant in acidic media under ambient conditions as previously described.^{14,24} Briefly, the Brij76 surfactant (8.0 g) was added to 400 mL of 1 M aq HCl while stirring. The covered mixture was maintained at 50 °C for 12 h prior to the addition of precursor. The surface-imprinted mesoporous organosilicas (TDMI-DEB and TDMI-BENZ) were prepared by adding the imprint surfactant, 4-decylaminetrinitrobenzene (0.5 g/400 mL), after Brij76 surfactant equilibration followed by an additional 6 h of equilibration at 50 °C with stirring. The addition of the imprint molecule gives the solution a yellow tint. This solution was filtered through 0.2 µm filter to remove excess imprint molecule. The filtered solution was returned to 50 °C and stirred for an additional 3 h prior to the dropwise addition of 1,3-bis(triethoxysilyl)benzene (22.6 g, 0.0562 mol) or bis(trimethoxysilyl)benzene (21 g, 0.0562 mol) precursor. To achieve the lower surface area imprinted DEB material, the stirring rate was significantly reduced (from 250–300 rpm down to 0–50 rpm) and the rate of precursor addition was increased from dropwise addition to 2 mL/s. The resulting solutions were stirred at 50 °C for 12 h and then aged at 70 °C for 24 h under static conditions. The precipitated yellow powders were then separated by vacuum filtration and refluxed in acidified ethanol (1 M HCl) for 12 h to extract the surfactant and imprint molecule. The powders were again separated by vacuum filtration and rinsed with ethanol. This extraction procedure was repeated twice, and after the final reflux, the resulting white powders were rinsed three times with deionized water and three times with ethanol. After drying under constant vacuum at 60 °C for 10 h, 13 g of nonimprinted BENZ, 12 g of imprinted BENZ, 12 g of nonimprinted DEB, and 9 g of imprinted DEB were recovered. Thermogravimetric analysis (TGA) confirmed the removal of surfactant and template imprint molecule.

Characterization. X-ray diffraction (XRD) measurements were made on an Enraf-Nonius FR591 rotating-anode using a bent graphite monochromator that selected Cu Kα radiation and provided in-plane resolution of 0.014 Å^{–1} full width at half-maximum. Powder samples were placed in 1.0 mm quartz capillary tubes. Gas sorption experiments were performed using a Micromeritics ASAP 2010. Nitrogen gas was used as the adsorbate at 77 K. Thermogravimetric analyses were performed with a TA Instruments TGA 2950 thermogravimetric analyzer. All measurements were made in high-resolution dynamic mode. A LEO 1455 scanning electron microscope (SEM) (Carl Zeiss SMT, Inc.) equipped with a tungsten filament was utilized to obtain scanning

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electron micrographs of gold sputter-coated (60 s at 5 psi) organosilica samples using a secondary electron detector, a beam voltage of 20.00 kV, a collector bias of 300 V, a 30.00 μm aperture, and a working distance of 15 mm. FT-IR spectra of each organosilica powder, sandwiched between AgCl windows, were acquired using a Bruker Tensor 27 FT-IR spectrophotometer.

TNT Preconcentration and Detection. Preconcentration and extraction experiments were performed using the sorbents packed into microcapillary columns placed in-line before an electrochemical flow cell. Sample volumes of 0.5–10 mL containing 5–1000 ppb TNT in a PBS buffer were preconcentrated in-line before the detector using microcolumns prepared by packing 10 mg of the organosilica material in a 100 μL glass column containing 1 mg of cotton on its displacing end. The electrochemical flow cell was obtained from BASi (West Lafayette, IN). The flow cell contained a carbon working electrode and a Ag/AgCl reference electrode. The glassy carbon working electrode was polished with an alumina suspension as suggested by the manufacturer. Buffer was allowed to flow through the apparatus for 30–60 min allowing the material to pack. To load the TNT sample, 0.5–10 mL of samples containing TNT (25–1000 ng/mL) was injected from low to high concentrations under a constant flow of 200 $\mu\text{L}/\text{min}$ using a syringe pump (model no. YA-12, Yale apparatus). Loading of TNT onto the column was evaluated electrochemically making sure that no TNT leached through the column. To elute TNT from the column, 500 μL of 40% acetonitrile (CH_3CN) and 60% PBS was injected at the same flow rate. TNT was detected electrochemically using square-wave voltammetry driven by a model 660 electrochemical workstation (CH Instruments, Austin, TX). A potential range of 0.3 to -0.8 V versus Ag/AgCl was scanned 200 times using square-wave voltammetry parameters of frequency = 100 Hz and amplitude = 25 mV to detect the first electrochemical reduction of TNT.³⁰ Distilled water was added to wash off the column in preparation of the next series of scans. The LOD was estimated from 3 times the standard deviation of the lowest concentration tested divided by the slope of the calibration curve of current versus concentration.

Adsorption from Contaminated Soil Extract. Archived soil (G55-X-A) taken from Umatilla Army Depot Activity, Hermiston, OR, provided by H. Craig (U.S. EPA, Region 10), was used to determine the relative effectiveness of DEB and TDMI-DEB for TNT adsorption from a heterogeneous environmental sample. Previous analysis of the soil showed soil TNT concentration to be 765 ppm.³¹ The soil (6 g) was equilibrated with 60 mL of distilled (DI) water on a rotary shaker for 16 h. The mixture was passed through a 0.2 μm PTFE Acrodisc filter. The organosilica sorbent (10 mg) was added to 10 mL of the filtered soil extract solution, and the resulting mixture was equilibrated for 1 h on a rotary shaker and then passed through a 0.2 μm filter prior to HPLC analysis. HPLC analysis was performed using U.S. Environmental Protection Agency Method 8330 with a Waters HPLC having dual 510 pumps and a 717 autosampler coupled to a photodiode array detector. The stationary phase was an Altech Altima C18 column with a 50:50 methanol/water mobile phase.

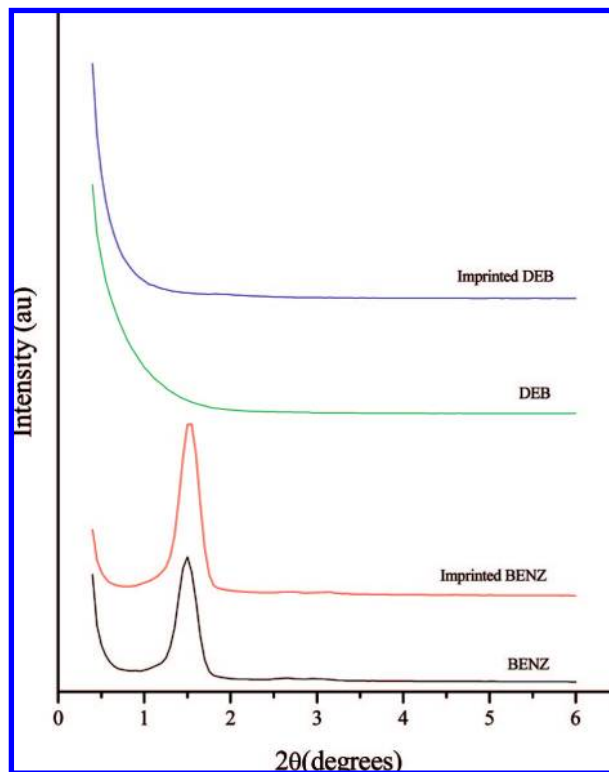


Figure 1. Powder XRD diffraction of imprinted and nonimprinted benzene (BENZ)- and diethylbenzene (DEB)-bridged hybrid organic–inorganic nanoporous organosilicas.

RESULTS AND DISCUSSION

Characterization of Materials. The synthetic route for the synthesis of TNT-imprinted and nonimprinted preconcentration materials was accomplished using Brij76 as the structure-directing surfactant to form a supramolecular template for subsequent polymerization of the 1,4-bis(triethoxysilyl)benzene (BENZ) or bis(trimethoxysilyl)ethyl)benzene (DEB) precursor, yielding a hybrid organosilica–surfactant structure. After extraction of the surfactant mixture as demonstrated by TGA (Figures S1 and S2, Supporting Information), a mesoporous organosilica powder was produced. Strong FT-IR bands in the 920–810 and 1110–1000 cm^{-1} regions confirmed the presence of Si–OH and Si–O–Si groups, while bands in the 1630–1400 and 900–675 cm^{-1} regions characteristic of the skeletal C–C stretching and out-of-plane C–H bending of aromatic groups were observed. (Figure S3, Supporting Information). For materials formed via template-directed molecular imprinting (TDMI-DEB and TDMI-BENZ), 4-decylaminetribenzene was mixed with the Brij76 prior to addition of the bistriethoxyorganosilane precursor. Powder X-ray diffraction patterns of the organosilicas are shown in Figure 1. As expected, the BENZ and TDMI-BENZ materials exhibit a (100) reflection, whereas no reflections were observed for the DEB and TDMI-DEB materials consistent with previous results which showed a well-ordered, hexagonally packed $P6mm$ structure for BENZ and a random pore structure for DEB.

Nitrogen sorption measurements performed on the imprinted BENZ material (BET surface area 980 m^2/g , total pore volume 0.714 cm^3/g) displayed type IV isotherms with large nitrogen adsorption capacities of 0.48–1.05 cm^3/g and sharp pore size

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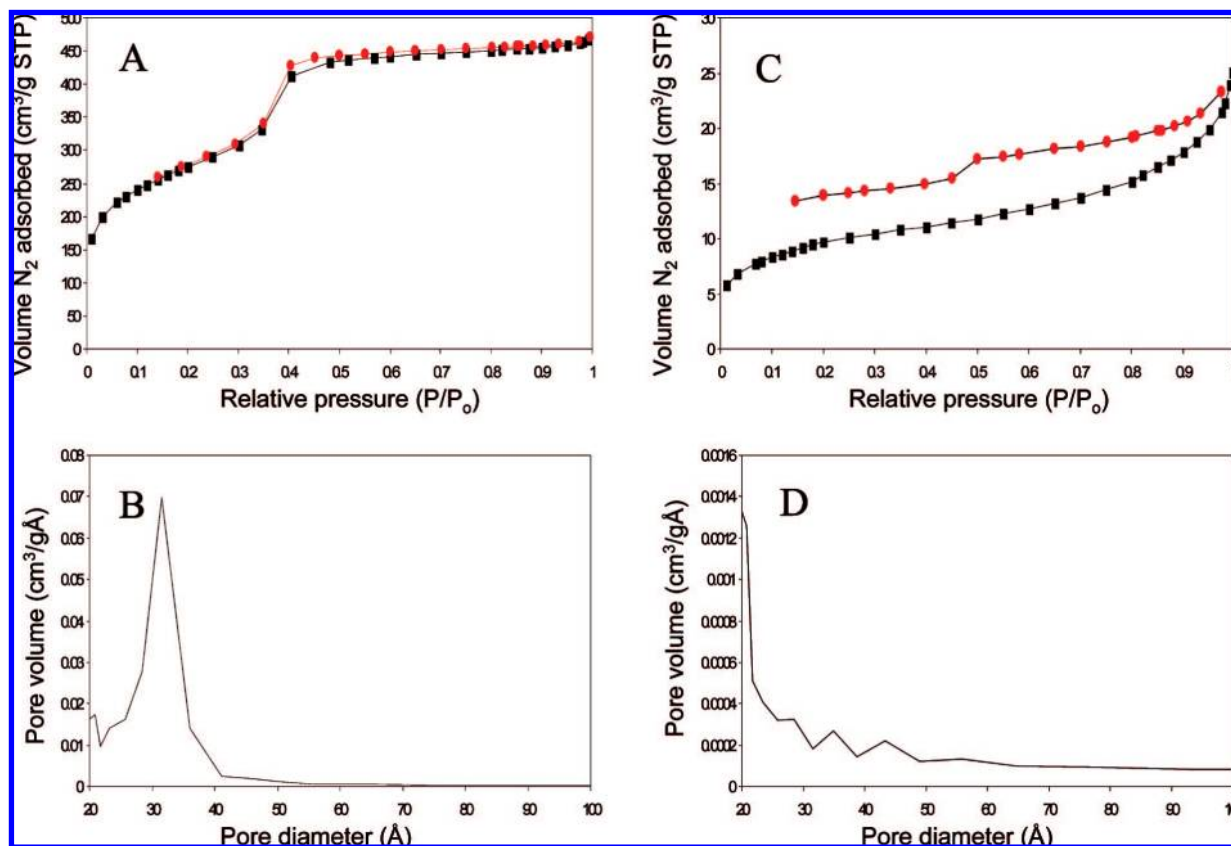


Figure 2. Nitrogen adsorption–desorption isotherm (A) and pore size distribution (B) for TDMI-BENZ, and nitrogen adsorption–desorption isotherm (C) and pore size distribution (D) for TDMI-DEB.

distributions (Figure 2). The isotherms displayed a large step in the mesoporous region and then flatten out to indicate a lack of any macropores. Nitrogen adsorption/desorption isotherms of the imprinted DEB material (BET surface area $35 \text{ m}^2/\text{g}$, single-point total pore volume $0.0331 \text{ cm}^3/\text{g}$) also yielded type IV isotherms with the adsorption branch exhibiting a linear region from $P/P_0 \sim 0.2\text{--}0.7$, characteristic of a broad pore size distribution in the mesoporous range (Figure 2). For comparison, nitrogen sorption isotherms of nonimprinted BENZ and DEB are shown in Figure S4, Supporting Information.

SEM of the materials (Figure S5, Supporting Information) revealed that each material consisted of particles with a broad size range. All of the particles ranged in size from $5\text{--}50 \mu\text{m}$. The DEB and TDMI-DEB particles were predominately $10\text{--}30 \mu\text{m}$, whereas the BENZ and TDMI-BENZ particles were predominately $5\text{--}15 \mu\text{m}$. The BENZ and TDMI-BENZ particles had a spherical morphology. In contrast, the DEB and TDMI-DEB particles had a nonspherical morphology.

Response Time and Limit of Detection. To investigate the effects of pore size distribution and imprinting on the response time and the LOD achieved by preconcentrating TNT using the imprinted BENZ and DEB sorbents, we used highly sensitive electrochemical techniques with a three-electrode electrochemical sensor. Sample volumes of $0.5\text{--}10 \text{ mL}$ containing $5\text{--}1000 \text{ ppb}$ TNT in a PBS buffer were preconcentrated in-line before the detector using a microcolumn containing 10 mg of an organosilica material. The TNT was rapidly eluted from the column using a $40\% \text{ CH}_3\text{CN}$ $60\% \text{ PBS}$ solvent mixture. Square-wave voltammetry was used to detect the reduction of TNT in an electrochemical

flow cell. An example of the resulting chromatovoltammogram is shown in Figure 3A. To create the chromatograms, peak currents from the first electrochemical reduction of TNT were plotted as a function of time from analysis of the 200 square-wave voltammograms generated during the experiment. Chromatograms of peak current versus time are shown in Figure 3B for the electrochemical detection of TNT at 1000 ppb using the mesoporous organosilicas to preconcentrate the sample.

The data illustrate the effects of the differences in preconcentration behavior of the imprinted BENZ sorbent, having highly ordered pore structures, and imprinted DEB sorbent, having an amorphous pore structure. When compared to the same concentration and volume of a TNT sample without a column, integration of the peaks in Figure 3B gave similar peak areas, suggesting that recovery of TNT from BENZ and DEB was near complete. More notably, the electrochemical response of TNT preconcentrated with the imprinted BENZ sorbent dramatically improved compared to an identical run with imprinted DEB. The impact of pore size distribution on preconcentration performance was particularly manifested in the superior desorption characteristics of BENZ sorbent with narrow pore size distributions relative to DEB which has a broad pore size distribution (Figure 3B). After preconcentration of the sample, the TNT was rapidly eluted from the column with the BENZ sorbent releasing the TNT faster than the DEB sorbent and displaying considerably less peak tailing.

As shown in Figure 4A, increasing TNT concentrations gave increasing linear responses in signal between 100 and 1000 ppb for all conditions tested. For TNT detection without using the preconcentration materials, we estimated the sensitivity, i.e., the

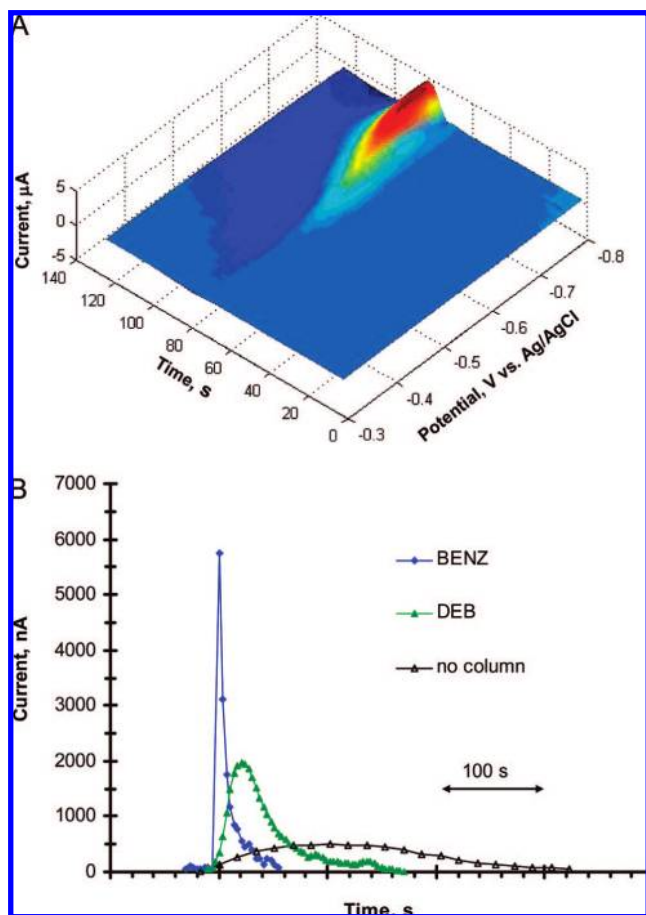


Figure 3. (A) Chromatovoltammogram using square-wave voltammetry of TNT (1000 ppb) at a glassy carbon working electrode. An amount of 500 μL of sample was preconcentrated in-line before the working electrode using a column packed with 10 mg of a nanoporous organosilicate (TDMI-BENZ). TNT was eluted off the column using a 40% $\text{CH}_3\text{CN}/60\%$ PBS solvent mixture. The square-wave voltammetry parameters are as follows: potential range = 0.3 to -0.8 V vs Ag/AgCl, frequency = 100 Hz, amplitude = 25 mV, flow rate = 200 $\mu\text{L}/\text{m}$. (B) Peak current vs time comparing imprinted BENZ and DEB for 1000 ppb TNT. Electrochemical parameters are the same as in (A).

slope of signal (nA) versus concentration (ppb) in our system to be 0.5 nA/ppb with an LOD = 130 ppb. When preconcentrating 500 μL of sample and comparing TDMI-BENZ to TDMI-DEB, TDMI-BENZ provided superior enhancement in sensitivity and improvement in the LOD owing to its more rapid elution of TNT from that material. For example, the slope of signal versus concentration for BENZ = 5 nA/ppb and for DEB = 1.7 nA/ppb, and the LODs were estimated to be 30 ppb for TDMI-BENZ and 90 ppb for TDMI-DEB. In addition, for TDMI-BENZ, the slope of signal versus concentration scaled linearly with increasing preconcentration volume (Figure 4, parts B and C), and for preconcentrating a 10 mL sample volume, the LOD for TNT was estimated to be ~ 5 ppb. Current electrochemical techniques for TNT detection using liquid chromatography or capillary electrophoresis with carbon³² and gold electrodes^{33–35} report LODs between 10 and 80 ppb. In addition when using square-wave

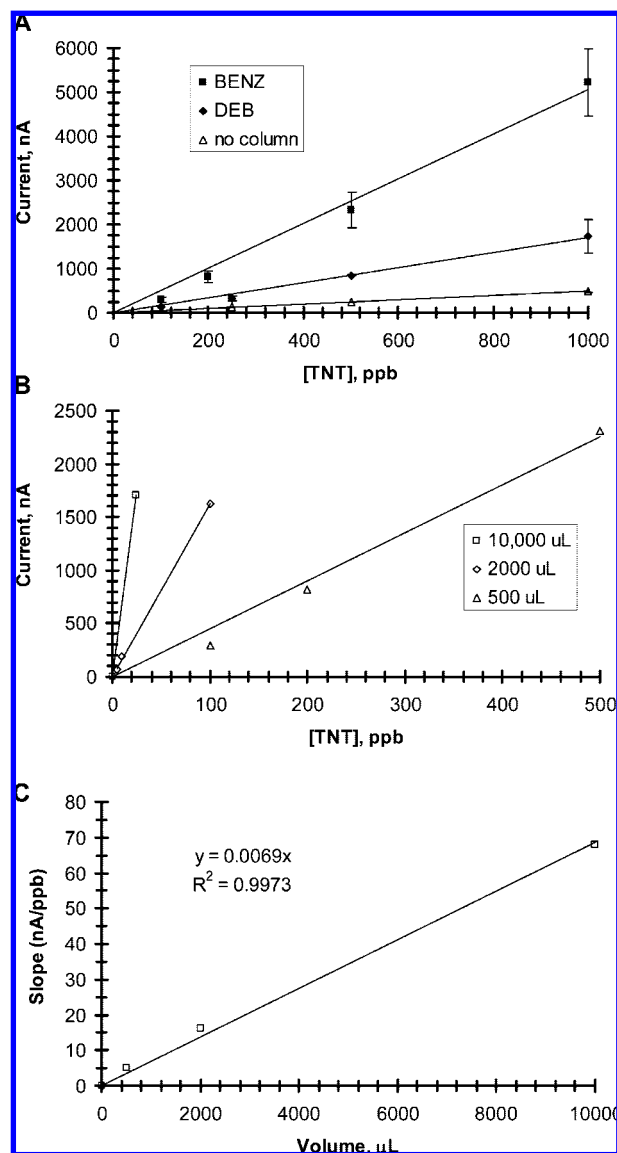


Figure 4. (A) Peak current vs [TNT] for the electrochemical detection of TNT using square-wave voltammetry comparing the TDMI-BENZ and TDMI-DEB material with and without preconcentration in-line before the detector. Preconcentration volume = 500 μL . (B) Peak current vs [TNT] comparing different preconcentration volumes using TDMI-BENZ. (C) Slope (nA/ppb) vs preconcentration volume using TDMI-BENZ. Electrochemical parameters are the same as in Figure 3.

voltammetry employing carbon electrodes, LODs between 25 and 200 ppb have been reported depending on the type of carbon and its preconditioning.^{30,36–38}

Adsorption from Contaminated Soil. Having examined the relative effects of pore size distribution on desorption behavior, we tested the relative adsorption of TNT from an aqueous extract of an archived soil sample (G55-X-A, Umatilla Army Depot Activity, Hermiston, OR). Both the soil and groundwater runoff from this soil are known to contain principally TNT (2,4,6-trinitrotoluene), RDX (1,3,5-hexahydro-1,3,5-trinitrohydrazine), HMX (1,3,5,7-hexahydro-1,3,5,7-tetranitrotriazine), Tetryl (*N*-2,4,6-tetranitro-*N*-

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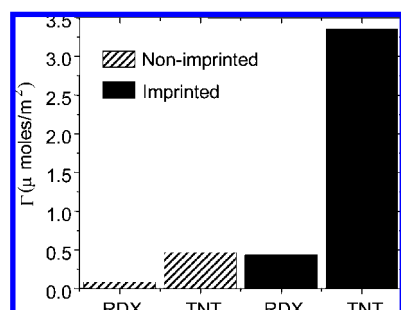


Figure 5. Relative adsorption of TNT and RDX by imprinted and nonimprinted DEB-bridged polysilsesquioxane.

methylaniline), 135TNB (1,3,5-trinitrobenzene), DNB (1,3-dinitrobenzene), NB (nitrobenzene), DNT (2,4- and 2,6-dinitrotoluene), and heavy metal ions such as lead, chromium, and cadmium.^{39,40} Since we were faced with a limiting factor for the creation of imprint sites due to the low solubility of our template imprint molecule (decylaminetrinitrobenzene) which at saturation gave less than a 5% ratio decylaminetrinitrobenzene to bulk surfactant (Brij76), low surface area and porosity imprinted DEB was used to enhance TNT selectivity. This choice was based on the premise that the total number of surface adsorption sites (S_T) is equal to the sum of nonimprinted (S_{nl}) and the imprinted (S_I) surface sites and that selectivity is increased as the total number of imprinted sites increases relative to the nonimprinted sites (i.e., increasing the ratio). Thus, we compensated for the low solubility of the imprint molecule and increased imprint site ratio by reducing total surface area (and thus total number of sites). The results are shown in Figure 5. Although both imprinted and nonimprinted DEB adsorbed TNT from the soil extract, the imprinted DEB significantly out-performed the nonimprinted DEB in terms of adsorption efficiency displaying a 7-fold increase in adsorption capacity for TNT. Additionally, TDMI-DEB was 4.5-fold more efficient in adsorption of the nonaromatic cyclic trinitroamine RDX although the overall adsorption capacity for RDX was much less than for TNT. TNT and RDX concentrations in the aqueous soil leachate were 218 and 138 μM , respectively. Similar increases in adsorption efficiency have been observed for template-directed molecularly imprinted organosilicas selective for organophosphonates.^{26,28}

For practical applications, another major component of soil runoff, dissolved organic matter (DOC), was considered. The composition of soil natural organic matter and the quality of DOC associated with soil leachate are complex and varying, and thus full quantification of its chemical makeup has been elusive. Although spectroscopic techniques such as NMR are desired in qualifying the specific attributes of DOC, methods which can be used as a relatively quick first approximation can provide meaningful results. UV spectroscopy has been shown to be useful in the relative assessment of bulk parameters such as hydrophobic content and aromaticity.^{41–43} Aromaticity is

Table 1. UV Absorbance Data for Soil Extract before and after Adsorption by Organosilicas

sample	absorbance at 250 nm	absorbance at 280 nm	absorbance at 365 nm	E_2/E_3
soil extract	1.932	1.147	0.410	4.72
post BENS adsorption	1.934	1.053	0.357	5.41
post imprinted BENS adsorption	1.952	1.085	0.371	5.27
post DEB adsorption	1.517	0.544	0.221	6.86
post imprinted DEB adsorption	1.826	0.763	0.315	5.80

particularly important because of the previously demonstrated influence of π – π interactions on the adsorption of aromatic phenols by DEB.²² Thus, to assess interferences and to gain a qualitative understanding of changes in DOC in the presence of imprinted and nonimprinted BENZ- and DEB-bridged organosilicas, we quantified the absorbance of solution at 280 nm and the quotient E_2/E_3 to assess the aromaticity of the soil solution before and after adsorption by the organosilica materials. The π – π^* electron transition occurs in this UV region for phenolic arenes, benzoic acids, aniline derivatives, polyenes, and polycyclic aromatic hydrocarbons which are thought to be common structural subunits of humic matter derived from terrestrial sources, and E_2/E_3 is the quotient of absorbances at 250 and 365 nm and has been found to correlate with the aromaticity of aquatic humic solutes.⁴² A reduction in absorbance at 280 nm and an increase in E_2/E_3 correlates with a reduction in aromaticity.

Table 1 shows the UV results for the soil extract solution before and after adsorption. The soil extract showed quite high absorbance at 280 nm and relatively higher at 250 nm with E_2/E_3 quotient = 4.72. The DEB-bridged organosilicas showed significantly higher reduction in aromaticity as illustrated by the 53% and the 33% reduction in absorbance at 280 nm for DEB and TDMI-DEB. This, in addition with the significant reduction in the E_2/E_3 quotient, clearly suggests significant interactions with a specific portion of the soil extract, namely, the aromatic portions. Note that when the much lower surface area of TDMI-DEB is taken into account, TDMI-DEB had higher inherent capacity for the reduction in the aromatic nature of the DOC. Thus, although imprinting did not reduce the amount of a possible interfering constituent such as DOC, from adsorbing, the fact that TNT adsorption increased after imprinting even in the presence of DOC suggests a higher capacity for TNT and the viability of the material in natural environments. In contrast, E_2/E_3 increase was approximately 15 and 12% for BENZ and TDMI-BENZ, respectively. Further, there was little difference in absorbance at 280 nm for the BENZ and TDMI-BENZ (maximum 8% reduction). The much smaller reduction in the solution aromaticity for the BENZ-bridged organosilicas, and hence interactions with aromatic portions of the soil extract, is consistent with the previously demonstrated relatively lower capacity for adsorption of BENZ for aromatic phenols in aqueous media as compared to DEB.²³

CONCLUSIONS

We have demonstrated that nanoporous organosilicas imprinted for TNT can effectively preconcentrate TNT in-line before

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an electrochemical detector and significantly lower its LOD. The ability to rapidly release TNT from the materials using CH_3CN significantly affected the performance parameters. The enhanced performance of BENZ compared to DEB most likely resulted from BENZ having a highly ordered pore structure compared to the amorphous pore structure of DEB. The ability to control structure in the synthesis of nanoporous organosilicas should give this class of material an advantage when tailoring important parameters in the design of new preconcentrating materials for a variety of different detection platforms and small-molecular-weight compounds. Furthermore, the imprinted DEB demonstrated significantly better TNT adsorption efficiency from an aqueous extract of contaminated soil than the nonimprinted DEB. These materials have the potential to improve existing methods used for trace detection, environmental monitoring, or laboratory analysis.

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SUPPORTING INFORMATION AVAILABLE

TGA, FT-IR, nitrogen sorption isotherms, and SEM of the materials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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