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14. ABSTRACT Titania nanotubes were produced in large quantities using hydrothermal synthesis. Short titania nanotubes and nanosheets were also produced based on various processing techniques. Based on systematic structural modeling we demonstrated that the structure of titania nanotubes is based on delaminated anatase along the [001] direction. For the first time, the x-ray diffraction pattern of titania nanotubes is successfully explained. This provides the basis for understanding the properties of decontamination of chemical warfare agents (CWAs). The anatase-like (001)					
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Report Title

Interactions and Reactions of Guest Molecules with Nanotubular Materials

ABSTRACT

Titania nanotubes were produced in large quantities using hydrothermal synthesis. Short titania nanotubes and nanosheets were also produced based on various processing techniques. Based on systematic structural modeling we demonstrated that the structure of titania nanotubes is based on delaminated anatase along the [001] direction. For the first time, the x-ray diffraction pattern of titania nanotubes is successfully explained. This provides the basis for understanding the properties of decontamination of chemical warfare agents (CWAs). The anatase-like (001) surfaces and the large surface area of titania nanotubes are quite attractive features for various surface chemistry based on theoretical studies. We used nuclear magnetic resonance to investigate the surface chemistry of titania nanotubes with a variety of small molecules such as catechol and methanol confirming the theoretical predictions. We evaluated the effectiveness of titania nanotubes for the decontamination of CWAs and achieved extremely positive results. In particular, this material is extremely effective in decontaminating VX, a CWA that has proven to be very difficult to remove in the past. Extensive tests have shown that titania nanotubes are air-stable and robust for decontaminating the commonly encountered CWAs with far better results than the currently employed products.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

1. "Decontamination of 2-chloroethyl ethylsulfide using titanate nanoscrolls" Alfred Kleinhammes, George W. Wagner, Harsha Kulkarni, Yuanyuan Jia, Qi Zhang, Lu-Chang Qin, Yue Wu. Chemical Physics Letters 411, 81-85 (2005).
2. "NMR study of water adsorption in single-walled carbon nanotubes" Shenghua Mao, Alfred Kleinhammes, and Yue Wu. Chemical Physics Letters 421, 513-517 (2006).
3. "Synthesis and Characterization of TiO₂ Nanotube/Hydroquinone Hybrid Structure" Yuanyuan Jia, Alfred Kleinhammes, Harsha Kulkarni, Kristopher McGuire, L.E. McNeil, and Yue Wu. Journal of Nanoscience and Nanotechnology 7, 458-462 (2007).
4. "Layered nanostructures of delaminated anatase: nanosheets and nanotubes" Gregory Mogilevsky, Qiang Chen, Harsha Kulkarni, Alfred Kleinhammes, William M. Mullins, and Yue Wu. Journal of Physical Chemistry C 112, 3239-3246 (2008).
5. "The structure of multilayered titania nanotubes based on delaminated anatase" Gregory Mogilevsky, Qiang Chen, Alfred Kleinhammes, and Yue Wu. Chemical Physics Letters 460, 517-520 (2008).
6. "Reactions of VX, GD and HD with Nanotubular Titania" George W. Wagner, Qiang Chen, and Yue Wu. Journal of Physical Chemistry C 112, 11901 – 11906 (2008).
7. "Molecules Immobilization in Titania Nanotubes: a Solid-state NMR and Computational-Chemistry Study" Q. Chen, Y. Jia, S.-B. Liu, G. Mogilevsky, A. Kleinhammes, and Y. Wu. Journal of Physical Chemistry-C 112, 17331-17335 (2008).
8. "Active anatase (0 01)-like surface of hydrothermally synthesized titania nanotubes" Qiang Chen, Gregory Mogilevsky, George W. Wagner, Jacob Forstater, Alfred Kleinhammes, Yue Wu. Chemical Physics Letters 482, 134-138 (2009).

Number of Papers published in peer-reviewed journals: 8.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

1. "Nanotubular Titania for Decontamination of Chemical Warfare Agents" George W. Wagner, Yue Wu, and Alfred Kleinhammes. Denver DECON Science & Technology Conference, December 2006.

2. "Titania Nanotubes and Organic-Inorganic Hybrid: Structures, Properties, and Applications" Yue Wu, Gregory Mogilevsky, Jacob H Forstater, Qian Chen, and George W. Wagner. RAHM08-Edinburgh July 2008.

3. "Titania Nanotubes and Organic-Inorganic Hybrid: Structures, Properties, and Applications" Yue Wu, Gregory Mogilevsky, Jacob H Forstater, Qian Chen, and George W. Wagner. ARO workshop Savannah Georgia, June 2009.

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Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):0

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Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):0

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Number of Manuscripts:0.00

Patents Submitted

Patents Awarded

Graduate Students	
<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
Harsha Kulkarni	1.00
Greg Mogilevsky	0.80
Yuan Yuan Jia	1.00
FTE Equivalent:	2.80
Total Number:	3

Names of Post Doctorates	
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FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Yue Wu	0.10	No
FTE Equivalent:	0.10	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

- The number of undergraduates funded by this agreement who graduated during this period: 0.00
- The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00
- The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00
- Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00
- Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00
- The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00
- The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Yuan Yuan Jia
Harsha Kulkarni
Greg Mogilevsky
Total Number:

Names of other research staff

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FTE Equivalent:	
Total Number:	

Inventions (DD882)

Titania nanotube is a new form of titania with unique morphology and local structures. It is an efficient porous sorbent material for a wide variety of organic molecules and exhibits unusually high decontamination efficiency for many chemical warfare agents (CWAs) including VX. Significant progress has been made in understanding the basic structure of titania nanotubes. This structure offers the largest surface area achievable of any TiO_2 structure with all Ti and O atoms exposed to relatively small guest organic molecules. This is a very desirable property for molecular absorption and catalytic reactions with guest molecules. What are the reaction mechanisms of CWAs with titania nanotubes? How could the reaction rates be improved? Answers to these questions require much detailed information on local structures and surface functional groups of titania nanotubes and related materials and significant progress has been made in this program in this area. Systematic study of local structures and properties of titania nanotubes under various synthesis and processing conditions has been carried out. A variety of techniques were employed for structural characterization such as microscopy, XRD, Raman, and NMR. NMR has been employed to study the details of important reaction processes such as dissociative and nondissociative surface hydration processes and reaction processes with CWAs and their simulants. To complement the experimental work, theoretical modeling of structures and reactions has also been pursued. These studies should have major impact on the development of decontaminants and self-decontaminating coating materials. This comprehensive study sheds light on the basic physical and chemical processes related to the interactions of CWA-related organic molecules with the nanoporous materials of titania nanotubes and derivatives. The close collaboration between UNC-Chapel Hill and U.S. Army Edgewood Chemical Biological Center ensured that the basic research carried out has had direct impact on the practical development in the area of CWA decontamination and mitigation.

Titania is a material of great interest due to its many unique properties, including catalytic and photoelectrochemical applications. Like most catalysts, the surface area and surface chemistry of titania are two of the most important factors that determine its properties. Neither would reach its maximum efficiency through the use of titania nanocrystals. In contrast, multilayered titania nanotubes are shown to achieve both the largest surface area and the unique surface chemistry to obtain the highest efficiency for certain chemical reactions including the decontamination of chemical warfare agents such as VX. Titania nanotube is a new form of titania. Figure 1 shows TEM and SEM images of titania nanotubes at various length scales. The TEM image in Fig. 1 (a) reveals the multilayered tubular structure with inner diameters of 5-6

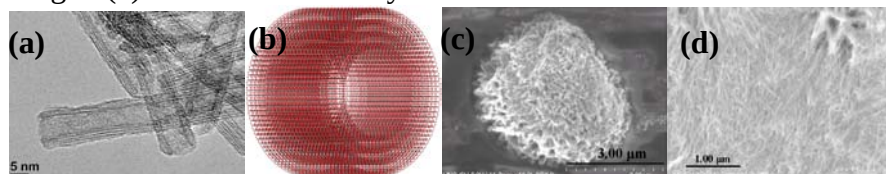


Figure 1: (a) TEM image of titania nanotubes revealing the multilayered tubular structure with inner diameters of 5-6 nm, outer diameters of 10-12 nm, and interlayer spacing of 8.7Å. (b) a structural model of multilayered titania nanotubes. (c) SEM image of a particulate of aggregated titania nanotubes. (d) Zoomed in SEM image of the particulate revealing the porous nature of the aggregated titania nanotubes.

nm, outer diameters of 10-12 nm, and interlayer spacing of 8.7Å. The model of such multilayered titania nanotube is shown in Fig. 1 (b). The SEM images in Fig. 1 (c) and (d) show how a typical particulate of aggregated micron-long titania nanotubes form into porous clusters. The aggregation of such tubular objects with high aspect ratios leads to particulates that are very

porous, preserving the intrinsically large surface area of titania nanotubes. This is in contrast to the aggregation of nanocrystals which pack densely and eliminate the effective surface sites necessary for chemical reactions. As we found out through our study, titania nanotubes are air stable for maintaining chemical reactivity. In our studies we made breakthroughs in understanding the basic structure of titania nanotubes and we demonstrated the extraordinary performance of titania nanotubes in decontaminating the CWA VX achieving a rate comparable to liquid decontaminants.

Titania Nanotubes There are two basic questions that are important for the development of nanostructured titania for catalytic applications. (1) What is the largest surface area achievable for TiO_2 without losing the characteristics of bulk TiO_2 ? (2) Does the surface area originate from the desired titania surface? It is particularly important to increase the surface area of surfaces with desirable properties. Theoretical and experimental evidences indicate that anatase (001) surface performs better for various chemical reactions. However, due to its large surface energy, the (001) surface is the minority surface in typical anatase nanocrystals. Here we explain the structure of multilayered titania nanotubes that have the highest achievable area of titania-like surface. Furthermore, the surface is exclusively anatase (001)-like.

The structure of anatase TiO_2 , as shown in Fig. 2 (a), is traditionally viewed as three-dimensional, in which the lengths of its apical bonds, all along [001], are longer than the equatorial bonds. This anisotropy could lead to delamination (such as by intercalation of Na^+ ions) along the [001] direction as illustrated in Fig. 2 (b). The multilayered delaminated anatase sheets could bend and roll up, as illustrated in Fig. 2 (c), into the nanotubular structure shown in Fig. 2 (d), analogously to graphene sheets and multi-walled carbon nanotubes.

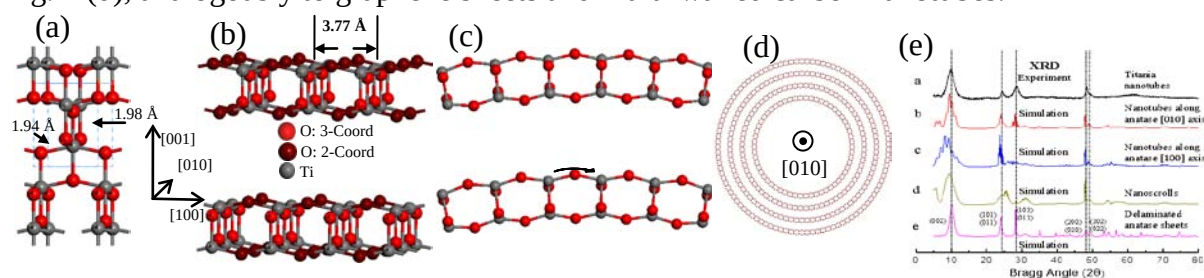


Figure 2: (a) Anatase unit cell. (b) Delaminated anatase with interlayer spacing of 8.7 Å. (c) Rolling of the delaminated anatase layers. (d) Formation of multilayered titania nanotube. (e) *a*. Experimentally collected XRD of titania nanotubes. *b*. Simulated XRD pattern of nanotubes rolled around the delaminated anatase [010] axis. *c*. Simulated XRD of nanotubes rolled around the delaminated anatase [100] axis. *d*. Simulated XRD of nanoscrolls, each formed by rolling up a single sheet. *e*. Simulated XRD pattern of delaminated anatase sheets.

We can synthesize this structure through a hydrothermal process as described later in detail in Task 1. This layered delaminated anatase structure possesses the highest possible surface area (including the intercalated space), $400 \text{ m}^2/\text{g}$, without losing the basic TiO_2 characteristics. Furthermore, because the direction of delamination occurs exclusively along the [001] direction, the surface is all anatase (001)-like; all Ti atoms are undercoordinated (fivefold rather than sixfold coordinated) and half of the O atoms are bridging oxygens (rather than threefold coordinated as in bulk anatase (Fig. 2 (b))).

A series of our experiments and computer modeling fully established the basic structure of titania nanotubes. The structure of delaminated anatase sheets (Fig. 1 (b)) provides the foundation for the structure of titania nanotubes. Figure 2 (e,a) shows the experimental x-ray diffraction (XRD) pattern of titania nanotubes. The simulated XRD pattern of delaminated

anatase sheets, shown in Fig. 2 (e,e), recreates all peaks observed in the actual experimental XRD (Fig. 2 (e,a)) along with other peaks that are not observed experimentally. The 10° peak corresponds to the interlayer distance. The creation of a true multilayered titania nanotube model is quite challenging unlike multilayered carbon nanotubes. After constructing various nanotubular and nanoscrolls models we now understand the basic structure of the nanotubes. Figure 2 (e,b) shows the simulated XRD pattern of nanotubes by rolling the double layers of delaminated anatase around the [010] axis. The experimental XRD matches the model excellently, including many detailed features. In contrast, Fig. 2 (e,c) shows the simulated XRD pattern of nanotubes formed by rolling the double layers of delaminated anatase around the [100] axis, this does not match satisfactorily with the experimental XRD. Figure 2 (e,d) shows the simulated XRD pattern of nanoscrolls by rolling a single layer of delaminated anatase. Again, the match with the experimental XRD is far from satisfactory due to the incorrect atomic registry along the [010] axis. The structure of titania nanotubes is highly ordered and the atomic registry between layers along the tube axis is preserved whereas it is lost along the circumference of the tube. This is fully expected since preserving the atomic registry between the layers along the circumference requires unrealistically highly strains bonds.

Although we do understand the basic structure of titania nanotubes at the level of XRD, properties such as structural relaxation and surface functionalization of titania nanotubes are far from obvious from XRD studies. Such structural information is important for understanding the surface chemistry. Raman, NMR and FTIR spectroscopy techniques have been used along with computational methods to assist the understanding of reaction processes in multilayered titania nanotubes.

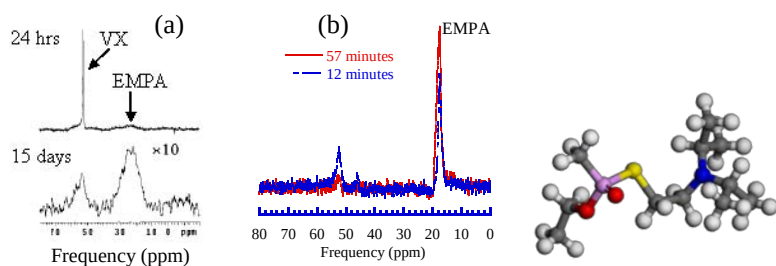


Figure 3: (a) ^{31}P NMR MAS spectra of 5 wt% VX added to AP- Al_2O_3 taken after reaction times of 24 hours and 15 days, respectively. (b) ^{31}P NMR MAS spectra of 5 wt% VX added to titania nanotubes taken after 12 and 57 minutes, respectively, after VX addition. (c) The proposed reaction scheme of hydrolysis.

Decontamination of CWA VX One of the known problems in the detoxification of VX by base-catalyzed hydrolysis in aqueous solution is the production of the stable toxic product S-(2-diisopropylaminoethyl) methylphosphonothioic acid (EA-2192). There is a significant benefit to employing solid oxide sorbents as VX decontaminant as due to the reaction selectivity no EA-2192 is produced [13-15]. Figure 3 (a) shows the ^{31}P NMR magic-angle-spinning (MAS) spectra of 5 wt% VX in AP- Al_2O_3 taken after a reaction time of 24 hours and 15 days. Here, the reaction product is the non-toxic ethyl methylphosphonic acid (EMPA, broad peak at 23 ppm). The toxic product EA-2192, which would give rise to a peak at 40 ppm, is absent. However, one of the major problems with this approach is the extremely slow rate of VX decontamination. Fig 3 (a) shows that the VX peak at 52 ppm is clearly visible even after 15 days! This problem is attributed to the non-catalytic function of the employed oxides in which the oxide surface is poisoned after the initial reaction. The reaction is further limited by the slow diffusion of VX

diffusion resulting from a high native viscosity and low vapor pressure. The ^{31}P MAS spectra in Fig. 3 (b) clearly shows that the reaction rate is much faster with titania nanotubes than with AP- Al_2O_3 (disappears after 1 hour rather than a month). The very sharp ^{31}P peaks in Fig. 3 (b) indicates that VX and the reaction product EMPA are quite mobile and are not bound to the surface. This supports the idea that the role of titania nanotubes in this reaction is catalytic in nature.

As described by the reaction scheme shown in Fig. 3 (c), water molecules are involved in the reaction process, the behavior of water on titania surface is also a topic of our investigation. Unlike on other surfaces, water is predicted to adsorb dissociatively on anatase (001) surface (Fig. 4). In titania nanotubes the Ti-O bonds are strained due to curvatures (Fig. 4(a) and 4(b)) and the effect of water dissociation is an important issue. We have investigated in detail water dissociation and reactions of small molecules with titania nanotubes by ^1H NMR. A comprehensive approach is used employing structural computation, XRD, Raman spectroscopy, and NMR. A computational approach at the DFT level (Gaussian, CASTEP, VASP) and force field level are proven to be very useful for studying structure and reaction processes as illustrated in Fig. 4 (c) and (d). Since titania nanotube is multilayered, it is important to know whether guest molecules can intercalate between the inner-layers of the nanotube (Fig. 4 (e)).

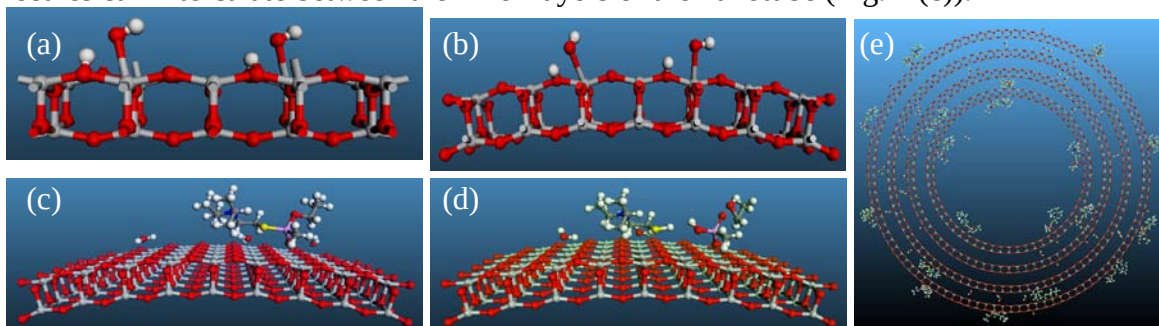


Figure 4: (a) Model of dissociative adsorption of water on anatase (001) surface. (b) Curved delaminated anatase layer where bonds are strained and could affect water dissociation. (c) and (d) illustrate models of surface reaction processes of VX on titania nanotube surface. (e) Illustration of where reactions could occur.

Our study shows that titania nanotubes are very efficient for CWA decontamination as shown in the table in Figure 5 below. It is clear that hydration has a huge effect on the half-life of CWAs. It is also very interesting to note that water improves the VX decontamination rate in titania nanotubes whereas it slows down the rate in anatase nanocrystals. In our studies we observed a gradual ^{31}P peak shift toward low field as the reaction time increased. This may be related to gradually increased intercalation. The vastly improved reaction rate in titania nanotubes is believed to be due to subtle placement of water molecules, self-catalyzed reaction via EMPA which is not chemically bound on surface as in Al_2O_3 , large surface area, and accessibility.

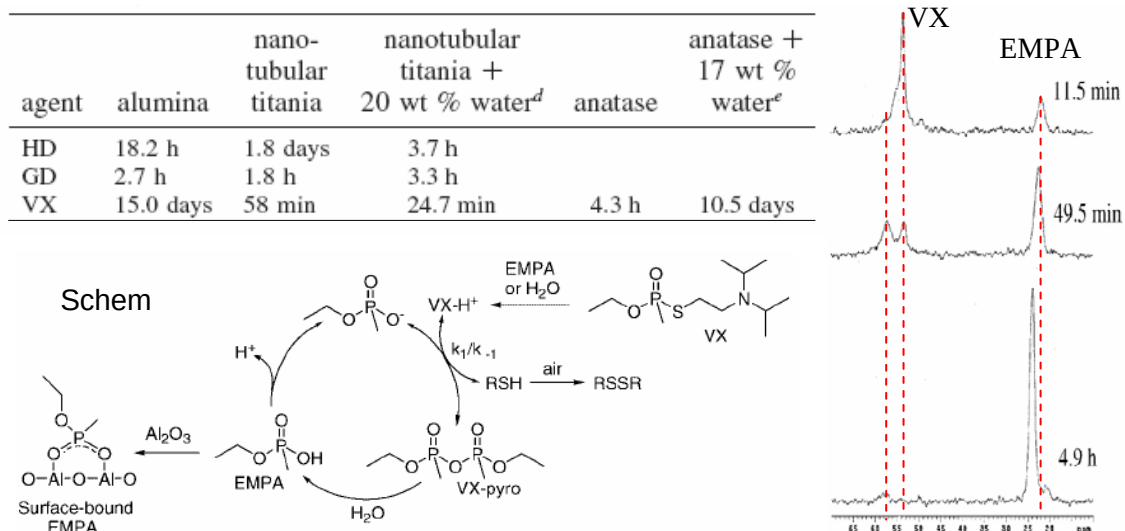


Figure 5: Table of half-life time of HD, GD, and VX in various decontaminants. An example of ^{31}P MAS NMR spectra of VX on titania nanotubes is shown along with the proposed reaction scheme.

In summary, we have demonstrated that titania nanotubes are very efficient for the decontamination of CWAs, especially VX. The detailed structures and surface chemistry are investigated by various analytical techniques such as NMR. It is shown that the surface of titania nanotubes are anatase (001) surface. The structure is based on delaminated anatase along the [001] direction. Different processing techniques have been applied to titania nanotubes to produce new structures such as titania nanosheets and to modify the surface chemistry. This study demonstrates that titania nanotubes can be developed into a very promising and practical product as decontaminant for chemical warfare agents.