$^{31}\text{P MAS NMR}$ – A Useful Tool for the Evaluation of VX Natural Weathering in Various Urban Matrixes

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### 4. TITLE AND SUBTITLE
31P MAS NMR A Useful Tool for the Evaluation of VX Natural Weathering in Various Urban Matrixes

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### 13. SUPPLEMENTARY NOTES
Contamination Risk Assessment

- Recent unconventional terror attacks:
  - 1995 Tokyo subway GB attack
  - 2001 US anthrax envelops
  - Numerous threats by various terror groups worldwide

- Unconventional Terrorism aimed at civilians:
  - Large population
  - Versatile ages and health conditions
  - Physically and mentally sensitive when compared to the military.
Major Goal: Help Defense Planners

- Analysis of the risk emerging from contaminated urban matrixes helps decide:
  - What to instruct population at the initial stage, after contamination
  - What to do with the contamination:
    » Let it weather naturally
    » Decontaminate actively (which decon and how much to use)
  - When it is safe to bring population back (full remediation)
Urban Area
(Matrixes Likely to be Contaminated)

- Plants
- Roads and Runways
- Roofs
- Soil / Sand
- Buildings and Pavements
Evaluation of Organic Matter on Matrix Particles

- **Extraction**
  - Need to find suitable solvent
    - e.g. heptane and toluene dissolve asphalt and bitumen
  - Sometimes requires additional steps
    - e.g. add base
  - Destructive

- **Solid State NMR**
  - In most cases involves no solvent
  - Carried out directly on particles
  - Not destructive; same sample is analyzed many times
  - Limited resolution
Related Published Works

- Reactions of VX, GB, GD, and HD with Nanosize Al$_2$O$_3$. Formation of Aluminophosphonates.
  Wagner et al., JACS 2001, 123, 1636-1644

- Preliminary Study on the Fate of VX in Concrete.
  Wagner et al., Langmuir 2001, 17, 4336-4341

- Effect of Drop Size on the Degradation of VX in Concrete.
  Wagner et al., Langmuir 2004, 20, 7146-7150

- $^{31}$P HR-MAS NMR Serves as a Convenient Tool for the Detection of VX Decay on Sand.
  Mizrahi & Columbus, poster presented at Decon 2002 Conference, San-Diego.
Materials

- Mediterranean sea sand
- Negev desert sand (including small rocks)
- Asphalt from local roads (ground by a ball mill)
  
  mean particle size=21.4 μm, SD=35.9%
- Bitumen-polymer sheets
- New concrete (manually crushed)
  
  mean particle size=27.6 μm, SD=15.4%
Experimental Method

- 500 MHz NMR (Bruker) equipped with a CP-MAS probe
- 4 mm rotor filled with powder (or a suitable piece of bitumen-polymer sheet), (ca. 100 mg)
- Matrix contaminated with ~99% VX (ca. 5 mg)
- $^{31}$P MAS NMR carried out using direct excitation (no CP) and high-power proton decoupling.
Sand Results or: What on Earth Is Soil?

Time “0” comparison between sea and desert sand

Sea sand

Desert sand

VX “endogenic” phosphate(s)
VX Degradation on Sea Sand

Phosphonate degradation product

3-4% S\(^-\) moiety
\(~75\) ppm

19 days
14 days
12 days
6 days
1 day

“0”
Unusual intermediate During VX Degradation on Sea Sand

Proposed Mechanism

\[
\text{Me} \quad \text{P} \quad \text{S}^- \quad \text{O} \quad \text{OEt} \\
\]

\[
\text{Me} \quad \text{P} \quad \text{S}^- \quad \text{O} \quad \text{OEt} \\
\]

\[
\text{N}^+ \\
\]

\[
\text{VX} \\
\]

\[
\text{Me} \quad \text{P} \quad \text{O}^- \quad \text{O} \quad \text{Et} \\
\]

\[
\text{Me} \quad \text{P} \quad \text{S}-\text{X} \\
\]

\[
\text{x}=\text{K salt (solution NMR)} \quad 71.51 \text{ ppm} \\
\text{x}=\text{K salt (spike on sand)} \quad 75.51 \text{ ppm} \\
\text{x}=\text{H} \quad 85.75 \text{ ppm} \\
\]

phosphonothiolate \( \sim 75 \) ppm

phosphonate

slow sand organisms
VX Degradation on Desert sand

Decreasing VX

Increasing phosphonate

Days

15

11

7

3.5

2.5

1.5

0.5

ppm
Fate of VX on Sand
A Comparison

![Graph showing the fate of VX on sand.](image-url)
Fate of VX on Sand

Different behavior of VX on sea and desert sand:

- VX degradation on desert sand:
  » Starts immediately and takes 18-24 days.

- VX degradation on sea sand:
  » Delayed for ca. 15 days (autocatalytic?)
  » High inconsistency between sea sand samples
    ■ Full degradation takes 26-70 days

Proposed explanation: sea sand contains salts:

- VX is less absorbed into sea sand;
- Peaks are sharper;
- Degradation is delayed and sometimes uncompleted.
Degradation of VX on Asphalt Powder

Decreasing VX

Increasing phosphonate

Two VX forms?

“0”
Fate of VX on Asphalt Powder

- VX degradation on asphalt powder is delayed for 15-25 days.
- Overall degradation process lasts 25-60 days.
- High inconsistency between samples, due to asphalt nature.
Degradation of VX on Bitumen-Polymer Sheet

Decreasing VX

Increasing phosphonate

Absorbed Form?

“0”
Fate of VX on Bitumen-Polymer Sheet

- About 10 days delay in VX degradation process.
- Small VX amounts still evident after 42 days.
Degradation of VX on Concrete

or: Does Israeli Concrete Obey Dr. Wagner’s Observations?

Increasing phosphonate

Decreasing VX

168
96
72
48
24
5
1

hours

100 90 80 70 60 50 40 30 20 10 0 -10 -20 ppm
Fast and active degradation, takes less than a week.
Conforms with previous observations for new concrete.
Conclusions - Method

- $^{31}$P solid-state NMR has been proven to afford reliable detection of VX on different matrixes.
- Experiments exclude the possibility of desorption.
- Since the method is non-destructive, samples were monitored repeatedly and degradation process easily normalized.

Method limitation:

- 2000 scans – down to 50 $\mu$g VX per sample
- Overnight experiment – down to 5-10 $\mu$g VX per sample
Conclusions - Operational

- One cannot predict the fate of CWAs on any complex matrix, due to:
  - an indefinite number of environmental matrixes
  - highly heterogeneous environmental matrixes
  - CWAs react chemically with most matrixes (beside the physical processes…)

- We propose looking at:
  - the most common matrix likely to face contamination;
  - general trends in behavior of similar matrixes;
  - taking worst-case-scenario as a recommendation for action, for untested matrixes.
General Trends for VX Fate or Matrix Families

Decontaminating I
Active, Fast
almost linear degradation

Decontaminating II
Slower
Follows one- or two-phase exponential decay pattern

Conserving
Slow degradation,
Following a delay
Thank You !!