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Chemical Warfare Agent and High Explosive Identification by Spectroscopy of Neutron-Induced Gamma Rays.

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Abstract

A non-destructive assay method to identify chemical warfare (CW) agents and high explosive (HE) munitions was tested with actual chemical agents and explosives at the Tooele Army Depot, Tooele, Utah, from 22 April 1991 through 3 May 1991. The assay method exploits the gamma radiation produced by neutron interactions inside a container or munition to identify the elemental composition of its contents.

The characteristic gamma-ray signatures of the chemical elements chlorine, phosphorus, and sulfur were observed from the CW agent containers and munitions, in sufficient detail to enable us to reliably discern agents GB [sarin], HD [mustard gas], and VX from one another, and from HE-filled munitions. By detecting of the presence of nitrogen, the key indicator of explosive compounds, and the absence of elements Cl, P, and S, HE shells were also clearly identified.

I. Introduction

Presently, CW munitions and storage containers are inspected and identified by direct sampling: in the case of CW armaments, a hole is drilled in the projectile and a small sample of the contents withdrawn for chemical analysis. Since the median fatal dose of nerve agents to adult humans is about one milligram[1], direct sampling of chemical weapons is potentially *lethal* if attempted in other than a controlled environment. Thus, the development of reliable *non-destructive* assay methods for CW agents *in situ* would greatly simplify the inspection and verification of CW inventories.

Table 1. Elemental composition, in weight%, of CW agents* and a high explosive**

	TNT	Sarin [GB]	VX	Mustard [HD]	Lewisite [L]
H	2.2	7.1	9.7	5.0	1.0
C	37.0	34.3	49.4	30.2	11.4
O	42.3	22.9	12.0		
N	18.5		5.2		
F		13.6			
Al					
P		22.1	11.6		
S			12.0	20.1	
Cl				44.7	51.3
As					36.1

*S. Budavari, ed., *The Merck Index*[1].
**R. Meyer, *Explosives*[2].

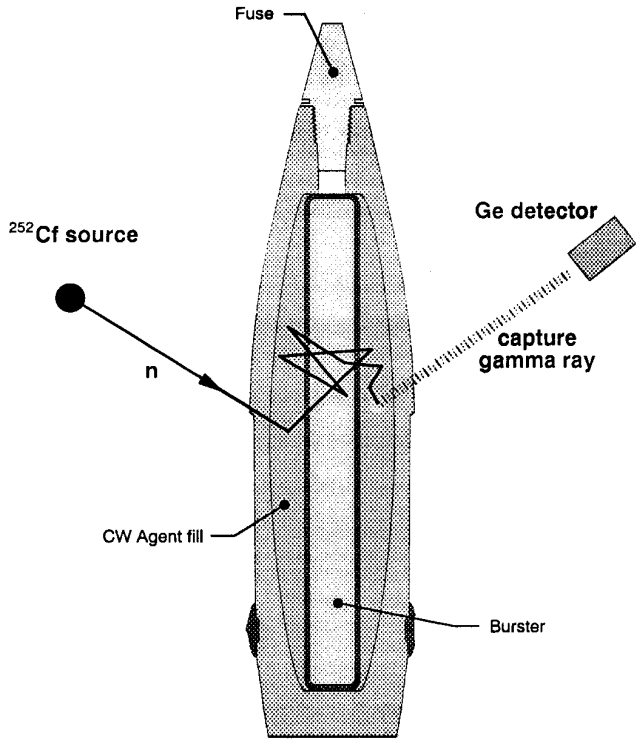

Fig. 1 Schematic neutron capture reaction

Non-destructive evaluation (NDE) of materials has been performed using various forms of penetrating radiation since the discovery of the x-ray at the turn of this century. In general, radiation assay methods are sensitive to the presence of individual chemical elements in an object, not their molecular combination. Both the CW agents[2] and the high explosives[3] used in munitions are organic chemicals, rich in carbon, hydrogen, and oxygen. However, each CW agent contains one or more of the elements chlorine, fluorine, sulfur, or phosphorus, in unique combinations, as listed in table 1. The latter chemical elements are absent in conventional high explosive munitions, as can be seen by comparison with the elemental composition of a typical military high explosive, also in table 1. Hence, an *elemental signature* will permit the detection and identification of CW agents or munitions with a high level of confidence.

Table 2. Selected Neutron Capture and Inelastic Scattering Gamma Rays*

Element	Type	Energy (keV)
Al	capture	984.0, 2959.8, 4132.9, 4252.2, 7723.9
	inelastic	843.8, 1014.4, 2211.8
As	capture	6294.1, 6809.4, 7019.2
	inelastic	264.6, 279.5, 572.5
B	capture	477.7
Ca	capture	1942.0, 4418.9, 6419.9
Cl	capture	516.7, 788.4, 1164.7, 1950.9. 1959.1, 2863.9, 5715.3, 6110.9, 6619.5, 7413.8
F	inelastic	109, 197.1, 1235.8, 1348.0, 1356.5
Fe	capture	352.2, 1725.1, 5920.3, 6018.5, 7631.1, 7645.5, 8886, 9298
	inelastic	846.8, 1238.3, 1408.2, 1810.5, 2112.9, 2598.5
Ge	capture	175.1, 596.4, 868.4, 3028.0
	inelastic	595.9, 743.2, 834.0, 867.9, 1039.5
H	capture	2223.3
N	capture	1884.8, 5269.2, 5298.0, 5553.4, 6322.4, 7299.1, 10829.
P	capture	2154.2, 3522.8, 3900.3, 4671.3, 6785.3
	inelastic	1266.1, 2233.4
S	capture	841.1, 2379.7, 2931.1, 3220.8, 4430.8, 4869.8, 5420.5
Si	capture	2092.9, 3539.1, 4934.4, 6380.7
	inelastic	1778.8

*Gamma-ray energies from the tables of Lone, Leavitt, and Harrison, and Demidov *et al.*, references 6 and 7.

Neutrons are an attractive probe of CW munitions and storage containers since they easily penetrate the thick steel casing of artillery projectiles and storage containers. Furthermore, the high-energy gamma rays from neutron-induced nuclear reactions can escape the container and provide identification of the chemical elements inside. Our assay technique measures the gamma rays produced by radiative neutron capture reactions and inelastic neutron scattering reactions within a munition or storage container to identify the elemental nature of its contents.

Neutron capture typically brings 7 to 10 MeV of excitation energy into a nucleus, from the difference in binding energies (hydrogen is an exception, with a 2.2 MeV binding energy). As the compound nucleus de-excites, multi-MeV capture gamma rays are usually produced, which can penetrate the container wall or shell casing. Since the capture gamma-ray energy spectrum differs for each chemical element, the energies and intensities of capture gamma rays can identify the elements within a container or munition. A neutron capture reaction within an artillery shell is depicted in figure 1.

While slowing down, neutrons also excite nuclei by inelastic scattering reactions. The excited nucleus promptly (in less than a picosecond) decays to the ground state with the emission of its characteristic gamma rays. Inelastic scattering reactions are useful for the assay of chemical elements with low neutron capture cross-sections.

The capture and inelastic gamma-ray spectra of all stable chemical elements have been measured and cataloged over the past 40 years, as important tools for basic and applied nuclear physics research[4-7]. Energies of the more intense capture and inelastic gamma rays from the indicator elements of CW agents, arsenic, chlorine, fluorine, hydrogen, phosphorus and sulfur, are enumerated in table 2. Also included in table 2 are gamma-ray energies for nitrogen, the indicator element for explosives, the elements found in structural materials, Al, Ca, Fe, and Si, and the elements Ge and B used in the radiation detector and its neutron shield.

II. Experimental Methods

The neutron source employed in the Tooele experiments is a two microgram californium-252 (^{252}Cf) fission source, producing about 10^6 neutrons per second. A 6"x 6"x 3" polyethylene block moderated the ^{252}Cf source and a bismuth "shadow-shield" blocked the HPGe detector from directly viewing the ^{252}Cf fission-product gamma rays.

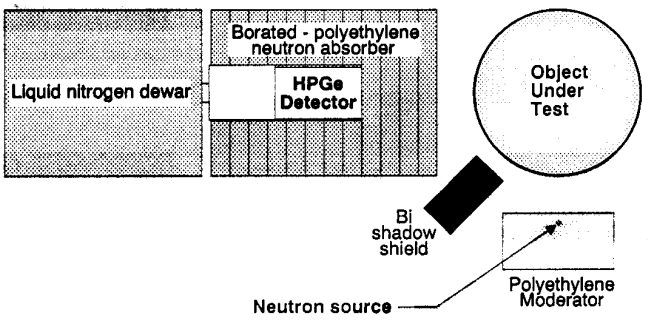

Fig. 2: Typical assay geometry.

Neutron-induced gamma rays were counted by a high-purity germanium (HPGe) detector. The detector is mounted in an all-attitude cryostat for portability, and it weighs 7 kg (15 pounds). For most of the measurements at Tooele, the HPGe detector was fitted with a borated-polyethylene neutron shield, to protect the Ge crystal from scattered neutrons; the neutron shield adds an additional 7 kg to the detector weight. The experiment geometry is shown in figure 2.

The pulses from the detector are amplified, sorted into energy bins, and stored with an EG&G Ortec Nomad Portable Multichannel Analyzer (MCA), coupled to a Zenith notebook-size PC. The computer displays the gamma-spectrum as it's acquired and serves as a flexible control panel for the instrument.

The energy resolution of the HPGe detector was checked with a Cobalt-60 source before, during, and after the Tooele tests to check for possible resolution degradation due to neutron damage or electronic noise. None was observed.

Details of the assay system equipment and operating procedures have been described elsewhere[8].

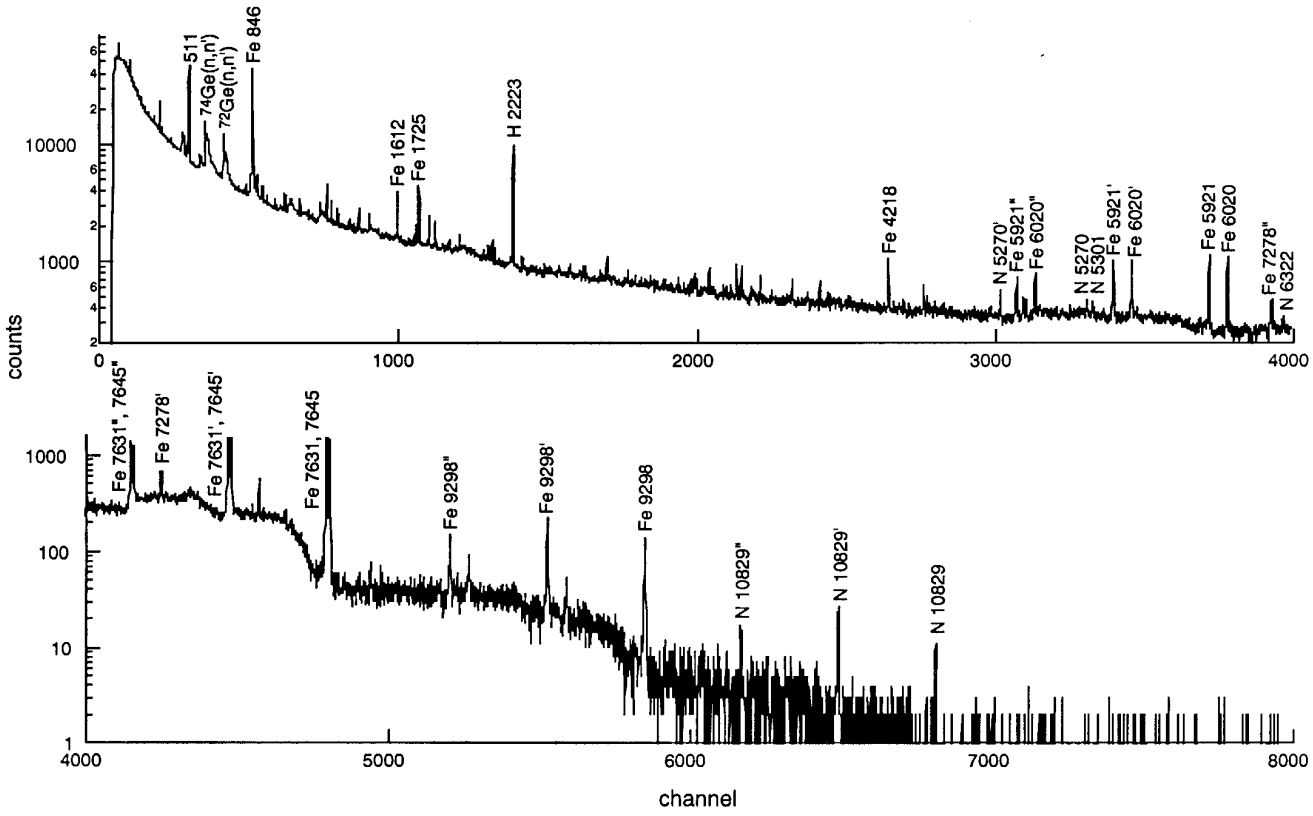

Fig. 3. High explosive gamma-ray spectrum

III. Test results

a. Tests with high explosive projectiles

The assay method was applied to 155 mm artillery projectiles, filled with composition B explosive, and 8 inch projectiles, filled with TNT. These measurements detected nitrogen and hydrogen capture gamma rays, as expected from explosives. Very strong iron capture gamma rays were also observed from the steel shell casing, and these lines are quite useful as a built-in energy calibration. The quality of the assay spectra may be judged from figure 3, the complete gamma-ray spectrum from neutron assay of a Composition B high explosive filled 155 mm artillery shell.

The high-energy portion of the HE gamma ray spectrum shown in figure 3 is compared with data from a VX-filled 155 mm shell in figure 4; note the almost complete lack of counts in the (lower) VX spectrum above 10 MeV (about channel 6300), while the (upper) HE spectrum displays prominently the 10829 keV nitrogen capture gamma-ray full energy peak, the single escape peak, denoted 10829', and the double escape peak, marked 10829".

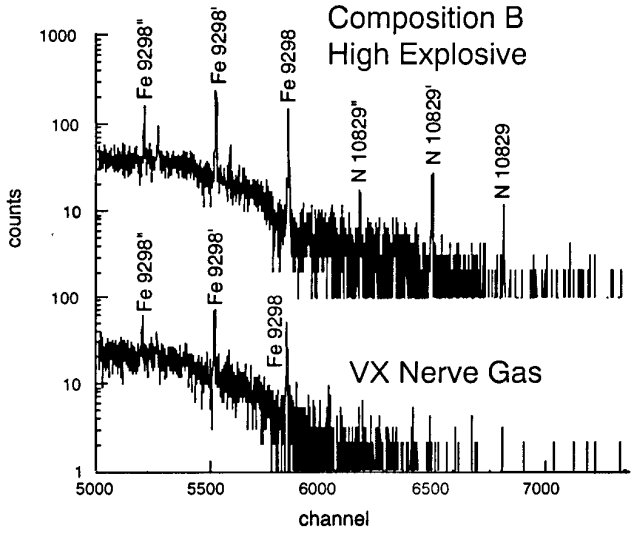

Fig. 4: Comparison of HE and VX gamma-ray spectra.

b. *Tests with CW agents*

Tests of our assay technique were performed on artillery shells, bombs, landmines, and ton containers filled with actual CW agents.

i. mustard gas [agent HD]

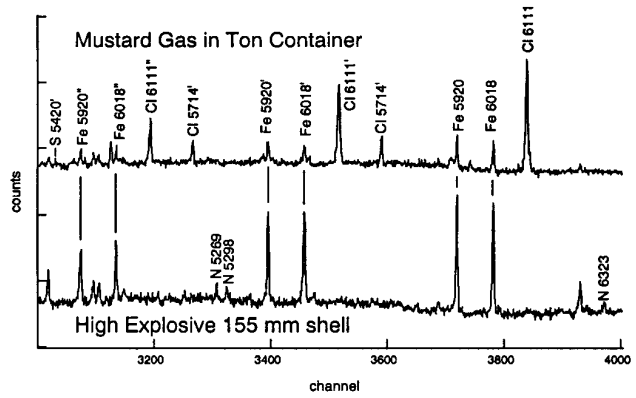

Fig. 5: Comparison of HD and HE gamma-ray spectra.

We have assayed three one-ton containers of mustard gas, and all three measurements yielded similar gamma-ray spectra, featuring strong chlorine capture gamma-ray lines, as expected. Sulfur capture gamma rays were also evident in these spectra.

ii. sarin [nerve agent GB]

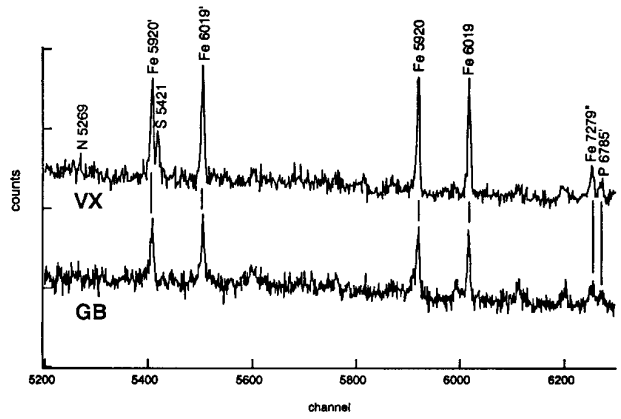

Fig. 6: Comparison of VX and GB gamma-ray spectra

Observation of the sulfur capture gamma ray is of particular importance since the presence or absence of sulfur uniquely distinguishes between mustard gas and lewisite. A portion of the gamma-ray spectrum from a mustard gas assay is compared with the same part of the spectrum from a high-explosive shell in figure 5; these spectra are easily distinguished.

Phosphorus capture gamma rays were observed in assays of GB-filled "weteye" aerial bombs, 155 mm artillery shells, and ton containers. Since the phosphorus thermal neutron capture reaction cross section is a factor of twenty lower than in the case of chlorine, the phosphorus peaks are less intense than those observed with the mustard gas containers, however they are sufficiently prominent for reliable identification after a 1000 second counting interval. The fluorine inelastic gamma rays were not observed in all GB spectra, however, even without this information, GB can still be distinguished from agent VX by the absence of sulfur gamma rays in the spectrum, as can be seen in figure 6.

iii. nerve agent VX

Phosphorous and sulfur are the indicator elements of agent VX. Capture gamma ray of both elements appear in the spectra of artillery shells, and land mines filled with this agent. To resolve the 5421 keV sulfur peak from the adjoining strong iron single-escape peak at 5409 keV, a high-resolution gamma-ray spectrometer is required. The good resolution of our HPGe spectrometer system can be seen in upper curve of figure 6, the capture gamma-ray spectrum from a shipping drum containing three VX-filled land mines.

IV. Conclusions

Table 3 Key chemical elements identified at Tooele

Fill	Container	Key elements present	Key elements observed
HD	ton container	Cl, S	Cl, S
VX	land mines	P, S	P, S
VX	155 mm shell	P, S	P, S
GB	weteye bomb	P, F	P, F
GB	ton container	P, F	P, F
GB	155 mm shell	P, F	P
TNT	8 inch shell	N	N
Comp. B	155 mm shell	N	N

A summary list of the key chemical elements identified in our measurements of various containers, munitions, and CW/HE fill materials is presented in table 3. Our criterion for reliable identification was the detection of two or more gamma-ray peaks for each key element, in order to avoid false positives.

The characteristic gamma-ray signatures of the chemical elements chlorine, phosphorus, and sulfur were observed from the CW agent containers and munitions, in sufficient detail to enable us to discern agents GB, HD, and VX from one another and from HE-filled munitions. The assay method detected the presence of nitrogen in the HE shells, the key indicator of explosive compounds.

Given the clear identification of the key indicator chemical elements by the assay technique, one may construct a simple algorithm for differentiation between the various of CW agents and high explosives, as shown in figure 7.

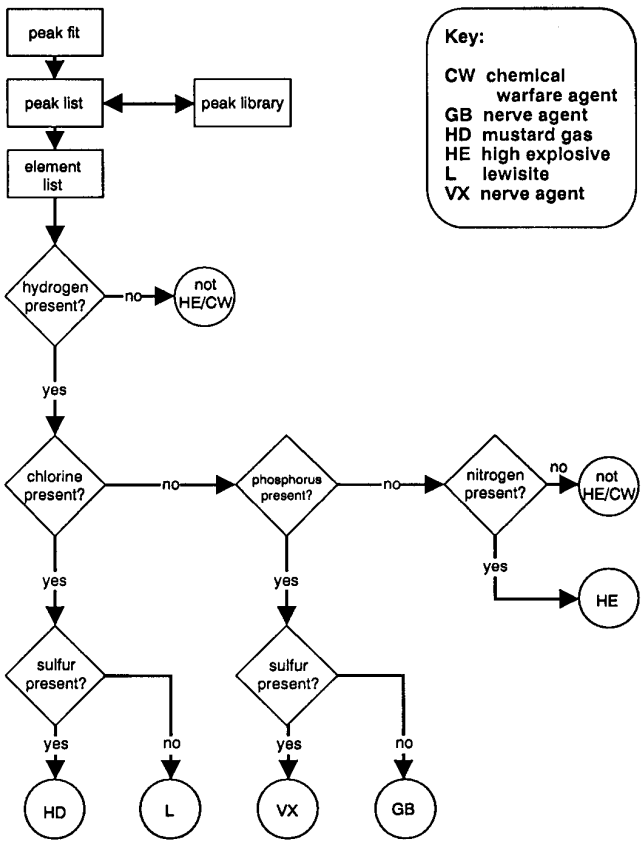

Fig.7: Identification algorithm

Most of the tests at Tooele were accomplished with a 1000 seconds (about 18 minutes) measurement time. With a stronger radioactive source and improved source moderation/shadow shielding, the measurement time can be reduced to perhaps 200 seconds or less. Indeed, due to chlorine's relatively large neutron-capture cross section, we have reliably assayed mustard gas (HD) in as little as 100 seconds with the present source and equipment.

The assay system was designed to verify declared stocks of CW agents and munitions. The successful test of this powerful assay technique suggests several additional applications, including challenge inspections, destruction facilities, and explosive ordinance disposal.

V. Acknowledgments

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VI. References

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