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Development of an analytical methodology for sarin (GB) and soman (GD) in various military-related wastes ☆

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Abstract

The Army requires analytical methods that can detect chemical agents down to the low part-per-billion (ppb) levels in their waste streams in order to meet various state regulations regarding the classification of hazardous waste. Analytical methods were developed for the measurement of sarin (GB) and soman (GD) at ppb levels that involved preconcentration of relatively large volumes (40–150 μl) of a chloroform extract onto a sorbent cartridge, followed by thermal desorption and analysis by GC–flame photometric detection. Certified reporting limits (CRLs) achieved with these methods ranged from 8.3 to 19 ppb for GB and from 1.8 to 5.3 ppb for GD in the three matrices screened. Method detection limits (MDLs) achieved with these methods ranged from 1.7 to 8.2 ppb for GB and from 0.39 to 1.2 ppb for GD. The methods are capable of achieving lower CRLs and MDLs with only minor modification. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Warfare agents; Soil; Environmental analysis; Validation; Sarin; Soman; Organophosphorous compounds

1. Introduction

The US Army, through its chemical agent testing and evaluation programs, generates considerable quantities of agent-contaminated wastes that have to be decontaminated before disposal. Several states regulate these wastes as hazardous wastes. If the Army could demonstrate to a given state that these wastes contain levels of chemical agents below a given threshold level, the Army could then petition the state to have such wastes reclassified, thereby substantially reducing their cost for disposal. The wastes described herein are associated with activities conducted at the Dugway Proving Grounds (DPG), Dugway, UT, USA.

An analytical methodology is described in this paper that was designed to achieve target reporting levels (TRLs) in the low parts-per-billion range for two nerve agents, isopropyl methylphosphonoflurori-date (sarin, GB) and pinacolyl methylphosphonofl-uoridate (soman, GD). TRLs were established at 0.024 and 0.006 for GB and GD, respectively, for fluids (μg/ml), soil (μg/g), and metal substrates (μg/g). In the absence of TRLs from the Army for

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this study, these TRLs were established on the basis of a simple, but conservative, human health risk assessment, which was conducted to support development of the analytical methodology. The assessment was based, in part, on interim toxicological criteria advanced by the Army [1]. The resulting TRLs represent the general range of lower concentration levels that are likely to be applied in a demonstration regarding the reclassification of hazardous waste as nonhazardous waste.

The general approach for these analytical methods is based on standard ''sorbent tube technology,'' which is routinely used for ambient air monitoring [2,3]. This technology involves the absorption of agents from large volumes of ambient air passing through a porous polymer sorbent cartridge, followed by their subsequent thermal desorption and analysis by gas chromatography (GC) coupled to such detection techniques as hydrogen flame ionization (FID), flame photometry (FPD), and mass spectrometry (MS), as well as others. This study employed the FPD method of detection, which was operated in the phosphorus mode. In this modification of the technique, which was first reported by Smith and Fowler [4], the chemical agents are extracted with chloroform from the various matrices, and an aliquot of this extract is injected onto the sorbent cartridge. Direct injection of chloroform solutions onto the porous polymer used in this work (Tenax TA) damages the polymer and invalidates the sample. Instead, the chloroform extract is injected onto a pre-column containing silanized glass wool. The chloroform and agent are volatilized as they pass through the glass wool, and only vapor is delivered to the sorbent cartridge. The polymer is unaffected by chloroform vapor, which passes through the sorbent cartridge, and the agent remains on the cartridge. To meet the TRLs, a relatively large portion (40–150 μl) of the extract is delivered to the cartridge. This approach is sufficiently versatile to achieve detection levels lower than those adopted in this work, if necessary. This approach achieves detection levels similar to those achieved with large volume, on-column injectors [5].

The performance of this approach for the agents and waste matrices considered was evaluated from a series of spike-recovery experiments for each separate agent–matrix combination [6]. After verifying the quality of the external calibration curves, a six-level series of experiments was conducted on each of four successive or nearly successive days. The spiking levels were chosen on the basis of the adopted TRL value. A ''certified reporting limit'' (CRL), defined in Ref. [6] and based on the approach of Hubaux and Vos [6,7], was computed from these data. In all cases, the CRL was less than the adopted TRL, and the methods are considered suitable for these applications. More details can be found elsewhere [8].

2. Experimental

2.1. Instrumentation

Analyses were performed using two Perkin-Elmer Model 9000 Autosystem gas chromatographs equipped with automatic thermal desorption (ATD-400) units. One GC system was dedicated to GB analyses, and the second system was dedicated to GD analyses. Both gas chromatographs were equipped with flame photometric detectors operated in the phosphorus mode. The two gas chromatographs were networked to two computerized data acquisition stations running Perkin-Elmer's Turbochrom software system. For each chromatograph, the GC column was a 30 m×0.53 mm I.D. DB-5, a film thickness of 1.5 μm. The programmed temperature profile started at 60 °C, ramped up to 90 °C at 10 °C/min, held at 90 °C for 1 min, ramped up to 220 °C at 45 °C/min, and held at 220 °C for 1.1 min. The carrier gas was ultra-pure helium at a flow-rate of 20 ml/min. The sorbent cartridges were desorbed at 250 °C for 5 min at a flow-rate of 80–100 ml/min to a focusing trap held at 0 °C. Desorption of analytes from the focusing trap was carried out at 250 °C for 4 min. The transfer line connecting the desorption unit and the gas chromatograph was maintained at 60 °C. In this study, the GC column was threaded through the ATD–GC transfer line and connected directly to the switching valve within the ATD.

Commercially available glass cartridges (Supelco; part No. 2-5090) were used for all spiking experiments. The cartridges were 4.5 in.×4 mm I.D. and packed with 90 mg of 60–80 mesh Tenax TA (1 in.=2.54 cm). The cartridges contained a glass frit at

the upstream end of the cartridge and a silanized glass wool plug and retainer spring at the downstream end. A strict quality-control program governed the use of these cartridges. Although the sorbent cartridges were reconditioned automatically in the analytical process of thermal desorption, the cartridges were reconditioned again by using a separate ATD unit at a temperature of 275 °C and a flow-rate of 80 ml/min for 1 h. In addition, 10% of the reconditioned cartridges were randomly selected and run as blanks.

2.2. Waste streams

Three types of waste were targeted for screening by the Army: substrates, which consist of bulk materials of various types; solids, consisting of soil and debris from cleanup actions; and fluids, consisting of previously used decontamination fluid. Unpainted steel disks, soil representative of DPG soil types, and a 5% high-test hypochlorite (HTH) solution in water were chosen as representative of these waste types.

Metal disks were prepared by the machine shop at DPG from 20 gauge, type 316 stainless steel, with a diameter of 0.25 in. and an average mass of 0.180 g. The disks were washed in a mild detergent solution and then rinsed with deionized water, methanol, and finally hexane. The disks were air-dried for 2 h and then oven-dried at 110 °C. The disks were used once and then discarded.

Two types of soil and decontamination fluid samples were used: NC, or noncontaminated, waste and SC, or suspect-contaminated, waste. The SC wastes were employed because they might contain by-products and degradation products of the agents that could interfere with the analysis. DPG personnel prepared a composite of representative DPG soils (DPG standard soil) with no known history of exposure to chemical agents; this sample was used as the NC soil matrix. The SC soil matrix was collected by DPG personnel from a solid waste management unit (SWMU) area at DPG in which GB and GD contamination is suspected. Both soil matrices were used "as is," without drying. The soil was screened to remove large pebbles, stones, and debris, and the larger soil clumps were crushed to reduce their size. The soil samples were dry when received in the laboratory and were sandy/gravel-like in nature, typical of soil found in a "desert-type" environment.

Finally, a decontamination fluid consisting of an aqueous solution containing 5–15% calcium hypochlorite was used. This fluid is generally prepared as a 15% slurry of HTH in water. HTH is a commercially available granular mixture containing 65% calcium hypochlorite. By the time the fluid is used to decontaminate test items and surfaces, it contains no more than 5% HTH. Therefore, a HTH–water (5:95) mixture was identified as representative of decontamination fluid waste. One-liter batches of aqueous 5% HTH solution, containing approximately 3.25% calcium hypochlorite, were prepared as needed by adding deionized water to HTH. To make the 5% HTH solution less hostile to the spiked chemical agents, the hypochlorite was completely neutralized by the addition of ascorbic acid. Two *M* NaOH was then used to adjust the pH of the reduced solution to 5.0 ± 0.1 to minimize hydrolysis of the GB or GD in spiked samples. Finally, a sufficient amount of saturated sodium chloride solution was added to bring the total volume to twice the volume of the initial 5% HTH solution, so that the overall dilution ratio is exactly 1:2. The solution was allowed to settle overnight and the supernatant decanted, leaving approximately 5% of the total volume behind as undissolved material. The resulting solution is referred to as the noncontaminated-filtered, reduced, pH-adjusted, and diluted (NC-FRPD) solution. The pH of the solution was checked each time a sample was removed for performing a set of spiking experiments and adjusted to pH 5.0 ± 0.1, if necessary.

Batches of SC decontamination fluid were prepared as needed by DPG Army-certified personnel by adding 12.5 g of GB to 1300 ml of 5% HTH solution and 12.5 g GD to 1100 ml of 5% HTH solution. The agent reacted rapidly with the hypochlorite, generating several degradation products. One agent was used in each batch. As a result, the SC decontamination fluid was known to have been exposed to the agent of interest before the analytical method validation experiments. Once prepared, this material was subjected to the same hypochlorite ion reduction, pH-adjustment, and dilution procedures described above for the NC decontamination fluid, except that the sediment was allowed to remain in the decontamination fluid. The resulting solutions,

one using GB and one using GD, are referred to as the suspect contaminated-filtered, reduced, pH-adjusted, and diluted (SC-FRPD) solutions.

2.3. Reagents

Isopropyl methylphosphonofluoridate (GB) and pinacolyl methylphosphonofluoridate (GD) were received as Chemical Agent Standard Analytical Reference Material (CASARM) from the Army Chemical Transfer Facility at Edgewood, MD, USA, and stored within the Chemical Repository at DPG. Army-certified personnel from DPG prepared both the agent calibration solutions and the matrix spiking solutions. The resulting ''dilute'' level stock solutions of each agent were prepared from CASARM stocks of neat agent and were transferred to the analytical laboratory for storage and use.

2.4. Calibration standard and spiking solutions

A set of eight calibration standard solutions for each agent was prepared in chloroform from CASARM reference standards. The standards corresponded to the following specified fractions of the TRL for each agent: 0, 0.375, 0.5, 1, 2, 5, 10 and 12.5×TRL. By selecting the proper spiking concentrations, solvent extraction volume, and volume of extract delivered to the sorbent cartridge, the same set of calibration solutions could be used regardless of the test matrix. Calibration was carried out by spiking 10 μl aliquots of the calibration standards onto sorbent cartridges and analyzing these cartridges as samples. In addition to the calibration standards, a check standard was prepared at a concentration corresponding to 8×TRL. The check standard was prepared from a different lot of neat CASARM by Army-certified personnel (other than those who prepared the stock calibration solutions). The concentrations of the GB and GD calibration and check standards are presented in Table 1.

Matrix spiking solutions were prepared at concentration levels corresponding to the following multiples of the TRL: 0, 0.5, 1, 2, 5 and 10×TRL. The same spiking solutions were used for all matrices. The solvent used for the spiking solutions was 2-propanol instead of chloroform to minimize evaporative changes in standard concentrations and for its compatibility with the aqueous HTH decontamination fluid used as one of the test matrices. Spiked samples of each matrix were prepared by applying 10 μl aliquots of the spiking solutions to 10.0 g samples of the metal and soil matrices and to 20 ml samples of the decontamination fluid. The concentrations of the matrix spiking solutions are described in Table 2.

During the spiking and extraction experiments, each sample was spiked with trimethylphosphate (TMP), in addition to the agent under investigation (GB or GD). TMP was used as a surrogate, a substance that is chemically stable but is similar in structure and behavior to both GB and GD and can be detected by FPD. TMP was always spiked at the 1×TRL level, regardless of the agent concentration. The surrogate peak in the gas chromatogram obtained from the analysis was examined visually and

Table 1
Calibration and check standard solutions for GB and GD

Standard type	Concentration level (Multiple of TRL)	GB standard concentration (ng/μl)	GD standard concentration (ng/μl)
Calibration	0×TRL	0.0	0.0
Calibration	0.375×TRL	0.18	0.045
Calibration	0.5×TRL	0.24	0.060
Calibration	1.0×TRL	0.48	0.12
Calibration	2.0×TRL	0.96	0.24
Calibration	5.0×TRL	2.4	0.60
Calibration	10.0×TRL	4.8	1.2
Calibration	12.5×TRL	6.0	1.5
Check	8.0×TRL	3.84	0.96

Note: 10 μl of each solution were used per spike.

Table 2
Matrix spiking solutions for GB and GD

Concentration level (Multiple of TRL)	GB spiking solution concentration (ng/μl)	GD spiking solution concentration (ng/μl)
0×TRL	0.0	0.0
0.5×TRL	12.0	3.0
1.0×TRL	24.0	6.0
2.0×TRL	48.0	12.0
5.0×TRL	120.0	30.0
10.0×TRL	240.0	60.0

Note: 10 μl of each solution were used per spike.

compared qualitatively with previous results to check for unusual matrix effects or gross errors in the spiking and solvent extraction steps of the analytical process.

2.5. Procedures

The spiking and extraction of the decontamination fluid was carried out by placing a 20 ml aliquot of the FRPD solution into a 40 ml conical centrifuge tube and adjusting the pH of the fluid to 5.0±0.1, the pH at which GB and GD have their greatest stability toward hydrolysis. A 10 μl aliquot of the surrogate spiking solution and a 10 μl aliquot of the desired agent spiking solution were dispensed into the pH adjusted FRPD solution. The centrifuge tube was immediately capped and the solution was swirled for 2–5 s. The extraction was then performed immediately by adding 2.0 ml of chloroform, capping the centrifuge tube, vortexing for 30 s, and then centrifuging at 2000 rpm for 2 min. A portion of the chloroform layer was retained for analysis.

Spiking and extraction of metal disks was done by placing approximately 10 g of metal disks into a 15 ml glass centrifuge tube. The surfaces of the disks were then spiked with a 10 μl aliquot of the surrogate spiking solution, followed by a 10 μl aliquot of the desired agent spiking solution. Immediately after the metal disks were spiked, 7.5 ml of chloroform was pipetted into the centrifuge tube, the tube was capped, and the solution was mixed by vortexing for 30 s. A portion of the extract was retained for analysis. A gas chromatogram identifying the recovery of a 2.4 μg spike of GB onto the metal disk substrate is presented in Fig. 1. The quantity of GB actually delivered to the column following the extraction procedure was found to be 47.8 ng, yielding a recovery of 99.6%.

Spiking and extraction of soil samples was done by placing approximately 10 g of soil into a 40 ml centrifuge tube. A 10 μl aliquot of the surrogate spiking solution and then a 10 μl aliquot of the desired agent spiking solution were injected onto the soil surface. After spiking, 7.5 ml of chloroform was pipetted into the centrifuge tube, the tube was capped, and the solution was mixed by vortexing for 30 s. The centrifuge tube was then centrifuged at 2000 rpm for 2 min. A portion of the unfiltered extract was then retained for analysis. A gas chromatogram identifying the recovery of a 60 ng spike of GD onto a soil substrate (NC) is presented in Fig. 2. The quantity of GD actually delivered to the column following the extraction procedure was found to be 1.3 ng, yielding a recovery of 108.3%. The doublet for GD in Fig. 2 represents the two isometric forms of GD associated with the asymmetric carbon in the pinacolyl-portion of the molecule. The two isomeric forms of GD associated with the asymmetric phosphorus atom are not resolved under the conditions of this analysis.

In all the spiking experiments described above, vortexing was found to be an essential step in the extraction of the spiked analyte, particularly for the metal disks. The metal disks, if not subjected to vortexing, tend to stack upon each other, thereby limiting the surface area available for extraction. Without vortexing, residual levels of analyte were detected on the metal disks during a second extraction. However, after the vortex step in each matrix extraction, no residual levels of analyte were

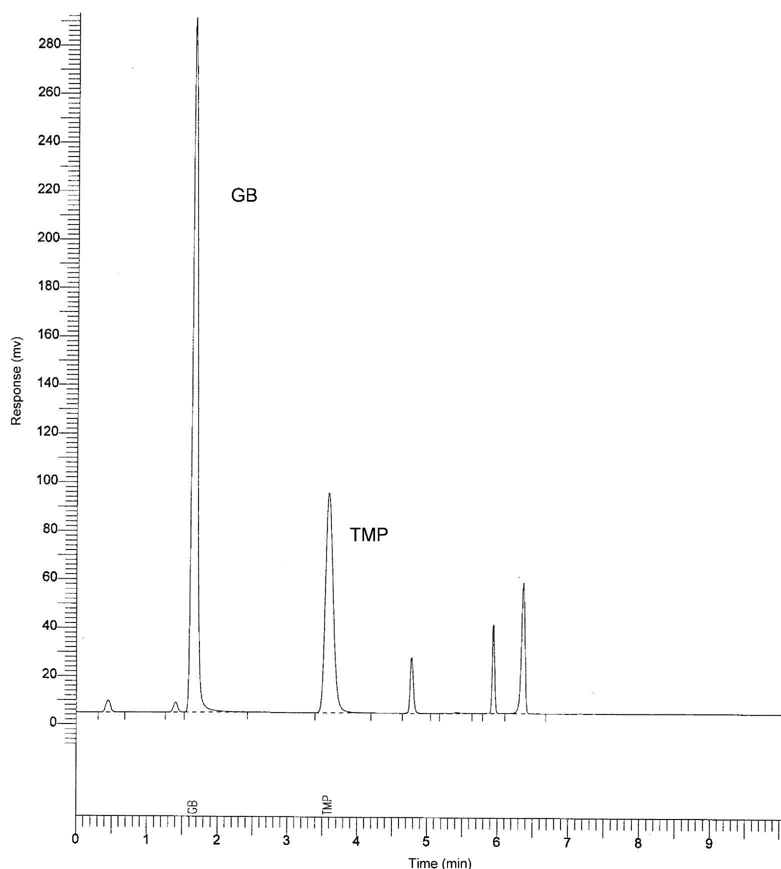

Fig. 1. Gas chromatogram for the recovery of a 2.4 μg spike of GB onto the metal disk substrate. The quantity of GB found amounted to 47.8 ng (actual value = 48 ng) yielding a recovery of 99.6%.

detected in subsequent extractions, under the conditions used for analysis.

Sorbent cartridges were prepared for analysis by transferring known amounts of chloroform extract to the cartridges. Since direct contact between the chloroform liquid and the sorbent resin bed must be avoided to prevent damage to the resin, all chloroform extracts and solutions were injected onto a silanized pre-column containing silanized glass wool. This pre-column, commonly referred to as a "fuzz tube," allows the solvent and extracted analytes to be volatilized on the surface of the glass wool before reaching the sorbent tube. The fuzz tube and sorbent cartridge were connected by using a standard PTFE plug valve. Each fuzz tube was used only once with the same glass wool packing. After each spiking procedure, the glass wool was removed and discarded. The empty sorbent tube was then cleaned with chloroform, acetone, and hexane, oven dried, re-silanized if necessary, and then repacked with silanized glass wool. Resilanization was determined by passing water through the tube and observing "beading" of the water droplets. If "beading" was not observed, the tubes were resilanized with trimethylsilyl chloride. The apparatus is illustrated schematically in Fig. 3.

After assembly, room air was passed through the system at a rate of up to 500 ml/min by applying a vacuum to the downstream end. An aliquot of the agent-containing chloroform extract was injected onto the glass wool in the fuzz tube. The amount of extract used depended on the specific matrix; 40 μl aliquots were used for decontamination fluid samples, and 150 μl aliquots were used for the metal and

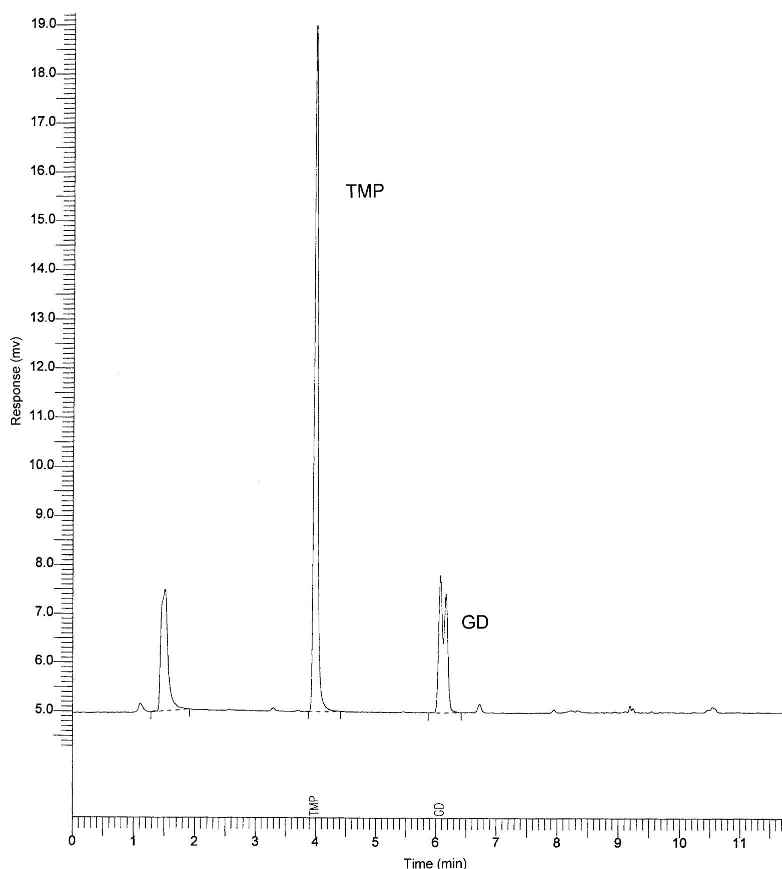

Fig. 2. Gas chromatogram for the recovery of a 60 ng spike of GD onto a soil (NC) substrate. The quantity of GD found amounted to 1.3 ng (actual value = 1.2 ng) yielding a recovery of 108.3%.

soil samples. After the extract was transferred, an additional 40 μl of chloroform was injected onto the fuzz tube to wash the tube and further promote the transfer of any residual agent to the cartridge. After allowing sufficient time for transfer of the agent onto the cartridge (approximately 5 min), the air stream was stopped, both ends of the cartridge were capped, and the cartridge was retained for analysis.

The approach described here offers several advantages over direct injection of the extract onto the GC column. Any nonvolatile material extracted along with the chemical agent remains on the fuzz tube and does not interfere with the analysis. The volume of extract that can be processed in this way is one to two orders of magnitude larger than the volume that could be injected directly into the GC and yields a corresponding increase in method sensitivity. This technique also provides a way to adjust the overall analytical method sensitivity to a wide concentration range and to very low (sub-ppb) levels.

3. Results and discussion

3.1. Method validation results

The methods described above were evaluated by using spike-recovery experiments, following guidelines initially specified by the Army [6] and extended as discussed below. Before the spike-recovery experiments, four calibration curves for each agent were generated and checked for linearity (F-test for lack of fit), a zero intercept (t-test for significance), and precision ($R^2 \geq 0.995$). Each calibration curve

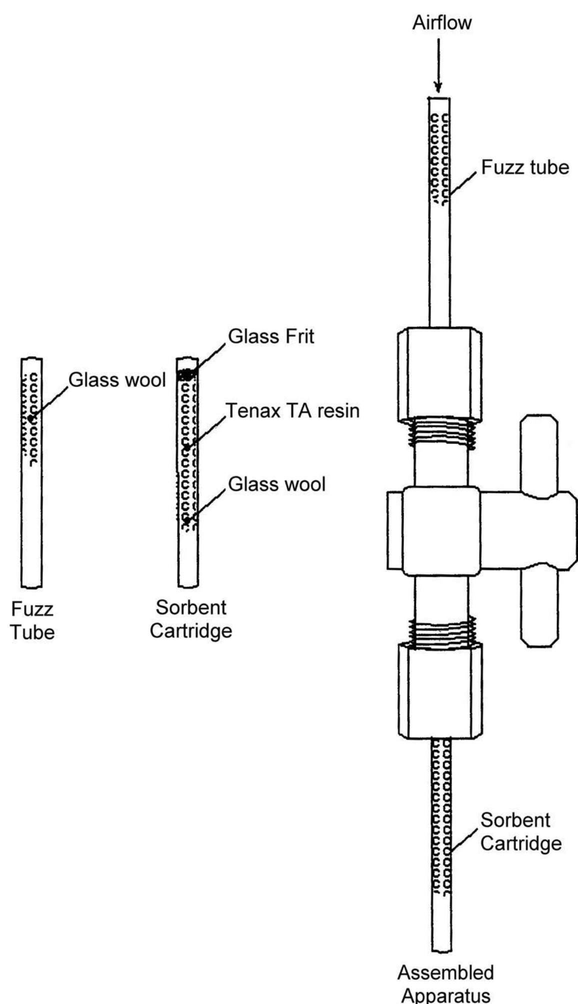

Fig. 3. Sorbent cartridge spiking apparatus.

was generated by using sorbent trap samples prepared according to the procedure described above. Seven samples were used, at spiking levels corresponding to 0.375, 0.5, 1, 2, 5, 10 and 12.5×TRL for the given agent. A typical calibration sequence is presented in Table 3. The calibration curves easily satisfied the acceptance criteria.

Four sets of spike-recovery experiments at selected spiking levels were conducted for each agent-matrix combination. Five spiking levels were used in each set, corresponding to 0.5, 1, 2, 5 and 10×TRL for the given agent. A matrix blank was also included in each run, as were two solvent spikes at the 1×TRL level, a matrix spike duplicate at the 10×TRL level, the high- and low-calibration standards, and a calibration-check standard at the 8× TRL level. The sample sequence for a matrix-spiked certification run is presented in Table 4.

Table 5 summarizes the results of a linear regression analysis of recovered versus spiked amounts of each agent in each matrix. The matrix blank results were included in the regression analysis as zero found amounts, which correspond to zero spiked amounts. Each regression analysis should then be based on 24 points, giving 22 statistical degrees of freedom. The GB-NCS and the GD-SCS results each contained an outlier, which was replaced by a computed replacement value. The motivation and procedures for identifying outliers and computing replacement values are discussed elsewhere [8].

All but one of the slopes listed in Table 5 are significantly higher than the ideal value of unity at the 95% confidence level.. These results indicate that the analyses produced concentration values that were systematically higher than the true values in all but one dataset. The intercepts are not significantly different from zero at the 95% confidence level All R^2 values exceed 0.995, and two exceed 0.999.

The reason for the apparent bias is not known. It is not clear whether this finding indicates a true positive bias in these methods or if there was some unknown problem with the technique or the instrumentation. Several potential problem areas were identified. The sample spiking and extraction procedures can be eliminated as the source of the problem because the solvent spike results, which involved no spiking and extraction steps, also gave systematically high percent recoveries for both GB and GD. Other possibilities include the following: the procedures used to prepare the agent stock and working stock solutions for both the calibration and matrix spiking solutions, possible memory effects caused by deposition of agent on various surfaces in the analytical train (ATD focusing tube, transfer line, and column, for example) and subsequent release over time (depending on usage), and variability in detector response caused by daily operation or changes in the laboratory environment (e.g., temperature, humidity, line voltage).

A CRL was computed according to Army guidelines for each agent–matrix combination [6]. One of

Table 3
Typical calibration run sample sequence

Tube no.	Calibration standard	Description
1	0×TRL	Sorbent cartridge spiked with 10 μl chloroform
2	0.375×TRL	Sorbent cartridge spiked at designated agent level
3	0.5×TRL	Sorbent cartridge spiked at designated agent level
4	1.0×TRL	Sorbent cartridge spiked at designated agent level
5	2.0×TRL	Sorbent cartridge spiked at designated agent level
6	5.0×TRL	Sorbent cartridge spiked at designated agent level
7	10.0×TRL	Sorbent cartridge spiked at designated agent level
8	12.5×TRL	Sorbent cartridge spiked at designated agent level
9	12.5×TRL	Sorbent cartridge spiked at designated agent level
10	0×TRL	Sorbent cartridge spiked with 10 μl chloroform
11	8.0×TRL	Sorbent cartridge spiked with check standard, independently prepared
12	Blank	Sorbent cartridge analyzed unspiked

the primary objectives of the method development program was to obtain CRL values no greater than the adopted TRL values. The CRL is a reporting limit computed according to the approach first introduced by Hubaux and Vos [7] and is identical to the detection limit defined by IUPAC [9]. Computations were carried out both independently and by using Army-supplied software. The variance of the spike-recovery results was assumed to be independent of spiking level (X,) and both false negative and false positive error probabilities were specified as 0.05. An explicit formula for the CRL under these assumptions is available in Currie and Svehla [9], for example. (Our notation differs from theirs in that our CRL is the same as their X_D.) An expression equivalent to theirs is:

$$\mathrm{CRL} = \frac{2}{1-g} \cdot \left(X_c - g\bar{X}\right) \tag{1}$$

in which X_c denotes the "critical value," given by:

Table 4
Typical method certification run sample sequence

Tube no.	Calibration standard	Description
1	Solvent control	2 ml chloroform spiked with 1×TRL of agent and 1×TRL of surrogate (TMP)
2	0×TRL	Matrix spiked with 10 μl of 2-propanol
3	0×TRL	Matrix spiked with 10 μl of 2-propanol
4	0.5×TRL	Matrix spiked at designated agent level
5	1.0×TRL	Matrix spiked at designated agent level
6	2.0×TRL	Matrix spiked at designated agent level
7	5.0×TRL	Matrix spiked at designated agent level
8	10.0×TRL	Matrix spiked at designated agent level
9	10.0×TRL	Matrix spiked at designated agent level
10	0.375×TRL	Sorbent cartridge spiked at designated agent level (low calibration standard
11	12.5×TRL	Sorbent cartridge spiked at designated agent level (high calibration standard)
12	8.0×TRL	Sorbent cartridge spiked with check standard, independently prepared
13	Solvent control	2 ml chloroform spiked with 1×TRL of agent and 1×TRL of surrogate (TMP)

Table 5
Linear regression results for GB and GD found versus spiked amounts

Agent	Matrix[a]	Slope[b,c]	Intercept[c,d]	(R^2)[b]	Degrees of freedom
GB	NCM	1.156±0.025	0.131±0.561	0.9976	22
	NCDF	1.088±0.014	−0.004±0.323	0.9991	22
	SCDF	1.031±0.026	−0.034±0.579	0.9968	22
	NCS	1.053±0.022	−0.065±0.499	0.9977	21
	SCS	1.119±0.030	0.280±0.677	0.9963	22
GD	NCM	1.140±0.012	−0.024±0.068	0.9994	22
	NCDF	1.000±0.030	0.052±0.169	0.9954	22
	SCDF	1.054±0.029	0.041±0.159	0.9963	22
	NCS	1.174±0.030	−0.003±0.170	0.9966	22
	SCS	1.078±0.023	0.053±0.129	0.9977	21

[a] NCDF = noncontaminated decontamination fluid; SCDF = suspect-contaminated decontamination fluid; NCS = noncontaminated soil; SCS = suspect-contaminated soil; NCM = noncontaminated metal.
[b] Dimensionless.
[c] The indicated uncertainties represent 95% confidence limits.
[d] Units = nanograms.

$$X_c = \left(\frac{ts}{b}\right) \cdot \left(1 + \frac{1}{N} + \frac{(\bar{X})^2}{S_{xx}}\right)^{1/2} \tag{2}$$

$$S_{xx} = \sum_{i=1}^{N} (X_i - \bar{X})^2 \tag{3}$$

X_i denotes the ith spiking level, and $\bar{X}$ denotes the average of the spiking levels used. The quantity g is defined by:

$$g \equiv \left(\frac{ts}{b}\right)^2 \cdot \frac{1}{S_{xx}} \tag{4}$$

The other quantities appearing are t, the 2-tail critical Student's t-value at the 90% confidence level for 22 (or 21) degrees of freedom; s^2, the residual sum of squares divided by the number of degrees of freedom; and b, the slope of the regression line for recovered versus spiked amounts.

In addition to the CRLs, method detection limits (MDLs) were computed according to US Environmental Protection Agency (EPA) guidelines, except that, for each agent–matrix combination, only four spike-recovery results were used instead of the mandatory seven for an ''official'' MDL [10,11]. The reported MDL values are equal to the standard deviations of the spike-recovery results at the lowest spiking level multiplied by the one-tailed 99% critical Student's t-value for three degrees of freedom (4.541). A summary of these results is given in Table 6, along with the relative standard deviation (RSD) at the TRL.

The CRLs listed in Table 6 clearly show a difference between GB and GD. This difference is attributed to the use of a different set of spiking levels for the two agents associated with the different TRLs used, combined with systematically lower standard deviations at lower spiking levels for both

Table 6
Summary of method validation results

Agent	Matrix[a]	TRL[b]	CRL[b]	MDL[b]	RSD[c] (%)
GB	NCM	24	15	8.2	19.0
	NCDF	24	9.2	2.2	2.3
	SCDF	24	18	3.7	3.5
	NCS	24	15	4.8	2.5
	SCS	24	19	4.4	7.8
GD	NCM	6	1.9	0.39	5.2
	NCDF	6	5.3	0.96	7.3
	SCDF	6	4.7	0.49	4.6
	NCS	6	4.6	1.2	7.9
	SCS	6	3.7	0.57	3.1

[a] NCDF = noncontaminated decontamination fluid; SCDF = suspect-contaminated decontamination fluid; NCS = noncontaminated soil; SCS = suspect-contaminated soil; NCM = noncontaminated metal.
[b] Units are ng/ml (ppb) for decontamination fluid, ng/g (ppb) for soil and unpainted metal.
[c] Method standard deviation at true concentration = TRL divided by TRL times 100%; dimensionless.

agents. This dependence of standard deviation on spiking level is a common observation in trace chemical analysis. The spiking levels are defined by Army guidelines in terms of the TRL value, and because the TRL for GD is one-fourth the TRL for GB, the corresponding spiking levels were also lower by the same factor. As a result, the standard deviation about regression is lower for GD than that for GB, and the computed CRL is also reduced by approximately the same factor.

However, outside of these obvious and explainable differences, the results do not show clear evidence of any significant difference in the performance of methods between matrices or between agents GB and GD. There are at least two reasons for this finding. One is that, after the sample extraction step, the analytical methods are virtually identical—they involve using the same preconcentration, thermal desorption, and GC stages and nearly identical equipment and operating conditions. Also, the extractions were performed as soon as possible after spiking the samples to ensure that the amount of agent present was accurately known. The second reason is that GB and GD are very similar chemically and are expected to behave in similar ways. Thus, the CRL values show no clear dependence on agent (between GB and GD only) or matrix type beyond that caused by the variation of method standard deviation with spiking level.

The CRL is computed from the set of experimental results and, as such, is subject to random statistical fluctuation. If the methods for a given agent are all essentially equivalent, the same CRL should be obtained for each matrix within statistical fluctuation, and the variability in the values listed in Table 6 should indicate the level of accuracy with which the CRL can be found. The standard deviation of the five CRL values divided by the mean CRL value equals 0.28 for GB and 0.33 for GD. Two other measures of the precision with which the CRL may be estimated were evaluated, a Jacknife analysis and a Monte-Carlo calculation, were carried out [8]. On the basis of these indicators, it appears that the CRL for these analytical methods can be found to within about 30% with a single determination by using four certification runs per dataset.

All MDL values are substantially less than the associated CRLs. Compared with the other GB values, the MDL for GB-NCM is unusually large because of an unusually large method standard deviation at the $0.5\times$TRL spiking level. The MDLs for GB and GD also exhibit a significant systematic difference, which is again caused by the combination of the lower spiking levels used for GD and the systematic increase of method standard deviation with spiking level. Because the lowest spiking level for GD was one-fourth of that for GB, the standard deviation of measurements at the lowest spiking level for GD, which is the basis for computing the MDL, was lower than that for GB.

Table 6 also lists the values of the method RSD at the $1\times$TRL spiking level. The computation of the standard deviation included measured values only; no outlier replacement values were used. A performance objective was that the RSD should be less than 10% for all agent/matrix combinations for spiking levels near the TRL. Excluding the two GB-NCM values at the 0.5 and $1\times$TRL spiking levels, the mean and standard deviation of the GB RSD values for all spiking levels and all matrices were 5.0% and 2.3%, respectively. The mean and standard deviation of the GD RSD values for all spiking levels and all matrices were 5.2% and 2.4%, respectively. The two datasets excluded in this summary had anomalously high RSDs due apparently to some temporary unidentified problem in spiking that was not repeated in the other runs.

3.2. Treatment of outliers

Because the presence of an outlier can distort the results of a statistical analysis, the identification of outliers is an important step in data review and analysis. The Army specifies that the dataset for each agent/matrix combination is to be examined for the presence of outliers. However, the procedure recommended by the Army, which is based on Dixon's "Q" test, was found to be problematic. An alternative procedure based on analysis of variance (ANOVA) techniques was used and gave good results. Details are available elsewhere [8].

3.3. Non-homogeneity of variances

The statistical procedures used in this study to evaluate method performance are all based on the

assumption that the variance of the replicate found values is the same for all spiking levels. However, it is common to observe that the standard deviation of measured concentrations in a variety of matrices and types of analysis increases systematically with the analyte concentration. This was also observed in this study. The principal effect is to cause the CRLs, computed using formulas that assume constant standard deviation, to be too large. CRLs computed in this way do not accurately reflect the performance of the analytical method at low analyte concentrations. This is also reflected in the observation that the MDLs for each method/matrix combination are systematically lower than the reported CRLs. More details are available elsewhere [8]. An alternative procedure for determining a detection or reporting limit using a weighted least-squares approach will be presented in a future paper.

4. Conclusions

The application of the Army's sorbent tube ambient-air-monitoring technology to the analysis of solvent extracted analytes for generating very low (ppb) detection levels appears quite feasible. Experimentally determined CRLs were less than the adopted TRLs for all agents and all matrices tested. Relative standard deviations averaged approximately 5% over all spiking levels for all agent–matrix combinations. The major advantages of this application are twofold: It allows a variable range of detection levels to be easily achieved with only minor modification of the sample volume, and the silanized glass wool pre-column serves as an excellent repository for any nonvolatile, co-extracted components that would otherwise be deposited on the analytical column. Even lower levels than those examined here can be reached by adjusting the amount of extract used, making this approach quite versatile.

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