GICHD Mine Dog Testing Project – Soil Sample Results #4

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Sandia National Laboratories

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Abstract

A mine dog evaluation project initiated by the Geneva International Center for
Humanitarian Demining is evaluating the capability and reliability of mine detection
dogs. The performance of field-operational mine detection dogs will be measured in test
minefields in Afghanistan and Bosnia containing actual, but unfused landmines.
Repeated performance testing over two years through various seasonal weather
conditions will provide data simulating near real world conditions. Soil samples will be
obtained adjacent to the buried targets repeatedly over the course of the test. Chemical
analysis results from these soil samples will be used to evaluate correlations between
mine dog detection performance and seasonal weather conditions. This report documents
the analytical chemical methods and results from the fourth batch of soils received. This
batch contained samples from Kharga, Afghanistan collected in April 2003 and Sarajevo,
Bosnia collected in May 2003.

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1.0 Introduction

The Geneva International Center for Humanitarian Demining (GICHD) initiated a project to evaluate the capability and reliability of mine detection dogs to find landmines in test minefields. Details describing the background, scope, objectives and project execution details can be found in the Terms of Reference (GICHD, 2000). The project seeks to evaluate weather data, surface soil sample chemical residue results, and mine dog performance to determine conditions optimal for successful landmine detection. Quarterly samples are planned for collection in two locations in Afghanistan (Kharga and Gardez) and two locations in Bosnia (Sarajevo and Mostar). Periodic reports will be produced documenting the results of samples submitted to Sandia National Laboratories. The first set of soil samples received by Sandia National Laboratories were obtained from two sites in Afghanistan prior to placement of the test landmines to determine if the sites contained explosive signature chemical residues that might confound future tests (Phelan and Barnett, 2001).

The purpose of this report is to document the surface soil chemical residue results from sample set #4 received at Sandia National Laboratories on June 9, 2003. The Swedish Defense Research Establishment (FOI) and the Geneva International Center for Humanitarian Demining (GICHD) collected these samples in Afghanistan April 2003 and in Bosnia May 2003.

Samples were packaged in an insulated cardboard box with plastic ice packs. Upon receipt, the temperature of the samples was measured by thermocouple and was found to be about 24°C and a number of the samples were damp. There is a potential, but unquantifiable probability, that degradation of the actual explosive concentrations in the soils occurred because of improper temperature maintenance during shipping. The samples were placed into a freezer at -10°C until sample preparation began on June 10, 2003. A total of 93 samples were received from Kharga, Afghanistan and 20 samples from Sarajevo, Bosnia. Sample analysis procedures were completed by June 26, 2003.

Sample preparation, extraction and quantification were performed using protocols developed for the US Environmental Protection Agency (EPA, 1998). Details on this method are described in Section 2. The analytical results are presented and discussed in Section 3.

2.0 Sample Analysis Method

Chemical residues of explosive related compounds in soils were analyzed using EPA Method 8095. The soil samples were received in 40 mL amber screw cap vials. The samples were mixed by vigorously shaking each vial. Approximately 0.8 g (± 0. 01 g) of soil was removed from each vial and placed into a 5 mL amber screw cap vial with care to avoid stones and organic material. A surrogate (25 µL aliquot of 10 mg/L of 3,4-dinitrotoluene) was placed into each extraction vial as a quality control check on

extraction efficiency. Acetonitrile (4 mL ± 1 mL) was added by pipetting to create a 4:1 solvent to soil ratio. A batch containing 20 samples was placed into a water bath cooled (10°C) ultrasonicator for 18 hours. The samples were then syringe filtered (0.45-μm nylon) and placed into an autosampler vial. The filtered soil extracts were analyzed by gas chromatography with a 1-μL autoinjection into a split/splitless injector containing a single taper liner (4-mm i.d. x 78-mm long). Primary column analyte separation used an RTX-5 column (Restek, 0.53-μm i.d., 15-m long, 0.1-μm film thickness) with a programmed temperature profile set for 70°C for 2 minutes, 10°C/min ramp to 200°C and then held constant at 200°C for 7 minutes. Confirmation analyses were performed using an RTX-225 column (Restek, 0.53 μm-i.d., 15-m long, 0.1-μm film thickness). The temperature profile for the RTX-225 was programmed for 100°C for 2 minutes, 10°C/min ramp to 200°C and then held constant at 200°C for 7 minutes. The electron capture detector was operated at 225°C for both column types with a nitrogen makeup of 60 mL/min.

Nine sets of 20 samples were prepared and each autosampler run schedule included the following vials:

> 1 each inlet passivation, 1000 pg/μL (all analytes),
> 3 each blank,
> 1 each continuing calibration verification (CCV),
> 1 each laboratory method blank (LMB),
> 1 each laboratory control standard (LCS),
> 1 each matrix spike (MS),
> 1 each matrix spike duplicate (SD),
> 5 each soil extract samples,
> 1 each continuing calibration verification (CCV),
> 5 each soil extract samples,
> 1 each continuing calibration verification (CCV),
> 5 each soil extract samples,
> 1 each continuing calibration verification (CCV).
> 5 each soil extract samples,
> 1 each continuing calibration verification (CCV).

Calibration standards of 5, 10, 25, 50, 75, and 100 pg/μL were prepared for each batch of samples. Table 1 shows a list of the analytes quantified and the acronyms used in this report. The analyte tetryl was added to the chemical analyses because of the presence of tetryl in a mine in one of the locations. Tetryl is challenging to analyze because chemical instability leads to larger analytical error and method detection limits. Quadratic fit calibration equations were used to quantify the peak area of the sample chromatograms. Figure 1 shows a calibration standard using the RTX-5 column and Figure 2 shows the same standard on an RTX-225 column.

Table 1: Analyte List

| Analyte	Acronym
1,3-Dinitrobenzene	DNB
2,6-Dinitrotoluene	2,6-DNT
2,4-Dinitrotoluene	2,4-DNT
3,4-Dinitrotoluene (surrogate)	3,4-DNT
1,3,5-Trinitrobenzene	TNB
2,4,6-Trinitrotoluene	TNT
Hexahydro-1,3,5-trinitro-s-triazine	RDX
4-Amino-2,6-Dinitrotoluene	4-A-DNT
2-Amino-4,6-Dinitrotoluene	2-A-DNT
Tetryl	Tetryl
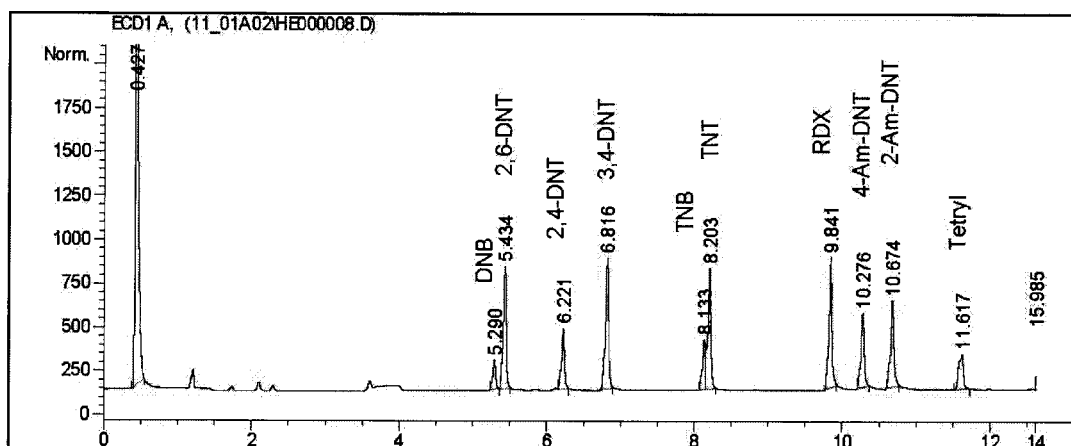
Figure 1: RTX-5 Column Chromatogram - 50 pg standard
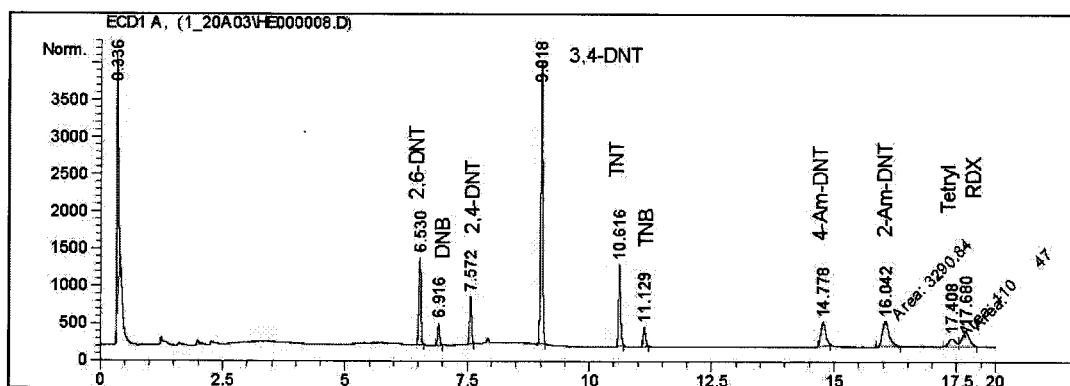
Figure 2: RTX-225 Column Chromatogram - 50 pg standard

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The Laboratory Method Blank (LMB) is an acetonitrile extract of an uncontaminated soil to evaluate the presence of naturally occurring interferents. The Laboratory Control Spike (LCS) is an uncontaminated soil spiked with the full list of analytes at 250 ng/g to evaluate bias in the soil extraction process. Both the LMB and the LCS used clean soil from Sandia National Laboratories. The Matrix Spike (MS) is similar to the LCS but used a randomly chosen sample from the suite of samples collected for analysis from the actual site. The Matrix Spike Duplicate (MSD) is used to assess variability of the analyte recoveries from the actual site matrix. The Continuing Calibration Verification (CCV) is a mid point calibration (50 pg/μL) standard placed every ten samples in the autoinjection run to monitor instrument drift.

3.0 Sample Results and Discussion

3.1 Quality Assurance/Quality Control Sample Results

Surrogate recovery values for 3,4-DNT were within the acceptable range for all soil samples. Laboratory method blank samples found 2,4-DNT, TNT and RDX on the RTX-5 column in separate sample sets (each in a different LMB sample), but not on the RTX-225 column. Peaks found on only one column (not confirmed by the second column) are considered artifacts and do not represent detection of that analyte. Recoveries on the Laboratory Control Samples were within acceptable ranges for all analytes.

The confirmation column is used to confirm the presence of an analyte found on the primary column. If the confirmation column did not find an analyte within ± 40% of the value reported from the primary column, then the presence of the analyte on the primary column was not reported.

3.2 Method Detection Limits

The Minimum Detectable Limits (MDL) for the analytes are shown at the bottoms of Table 2 and were determined from soil obtained at Sandia National Laboratories (SNL) in Albuquerque, New Mexico, USA. All of the analyte MDLs, except for tetryl, were determined in February 2000. The MDL for tetryl was determined in this effort using both the SNL soil and the Kharga, Afghanistan soil. The tetryl MDL for the combined data set are also shown at the bottom of each page of Table 2. As expected, the tetryl MDL is about ten times greater than for the other analytes. The MDL values shown in Table 2 will probably be similar to values that would be found for the Afghanistan soils because the SNL and Kharga soils are both sandy loam soils. Soils with greater organic carbon, clay size fraction or other extreme properties would likely show different results and would need to be specifically evaluated.

3.3 Sample Results

Table 2 shows the sample results for the all analytes with acceptable quality control results identified.

Table 2: Qualified Sample Results (ng/g)

	2,6-DNT	DNB	2,4-DNT	TNT	TNB	4-Amino-DNT	2-Amino-DNT	RDX	Tetryl
Kharga April-03 Serie:3 10	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 11	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 15	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 17	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 18	U	U	30.1	U	U	U	U	U	U
Kharga April-03 Serie:3 20	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 27	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 29	U	U	U	17.4	U	36.9	50.3	U	U
Kharga April-03 Serie:3 30	U	U	U	32.1	U	92.8	124	45.9	U
Kharga April-03 Serie:3 32	U	U	U	U	U	U	U	23.8	U
Kharga April-03 Serie:3 35	U	U	U	U	U	U	U	54.4	U
Kharga April-03 Serie:3 42	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 43	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 46	U	U	U	U	U	U	U	15.5	U
Kharga April-03 Serie:3 48	U	U	U	U	U	U	U	15.9	U
Kharga April-03 Serie:3 49	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 50	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 52	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 53	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 53	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 56	U	U	U	U	U	U	U	23.9	U
Kharga April-03 Serie:3 57	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 58	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 60	U	U	U	6.5	U	153	77.5	U	U
Kharga April-03 Serie:3 61	U	U	255	33.1	U	128	85.5	U	U
Kharga April-03 Serie:3 63	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 64	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 66	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 68	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 72	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 75	U	U	47.3	U	U	U	U	37.5	U
Kharga April-03 Serie:3 77	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 81	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 82	U	U	U	5.7	U	U	U	41.3	U
Kharga April-03 Serie:3 82	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 85	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 91	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 92	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 94	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 101	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 102	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 103	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 106	U	U	U	U	U	U	U	U	U
MDL (95%)	6.2	8.6	5.3	5.9	32.3	4.2	6.7	13.1	48.0
U-undetectable									

Table 2 (continued)

	2,6-DNT	DNB	2,4-DNT	TNT	TNB	4-Amino-DNT	2-Amino-DNT	RDX	Tetryl
Kharga April-03 Serie:3 108	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 110	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 112	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 117	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 119	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 121	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 123	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 125	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 126	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 128	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 132	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 134	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 135	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 137	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 138	U	U	U	5.8	U	U	U	U	U
Kharga April-03 Serie:3 139	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 142	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 143	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 144	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 145	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 146	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 147	U	U	U	5.1	U	U	U	U	U
Kharga April-03 Serie:3 148	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 149	U	U	U	24.3	U	U	U	U	U
Kharga April-03 Serie:3 151	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 152	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 153	8.3	19.3	291	19.1	38.4	22.8	8.3	7.4	U
Kharga April-03 Serie:3 157	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 158	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 163	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 164	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 167	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 172	U	U	U	U	U	234	172	1288	U
Kharga April-03 Serie:3 173	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 174	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 177	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 180	U	U	U	U	U	U	U	13.7	U
Kharga April-03 Serie:3 181	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 183	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 184	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 185	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 187	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 190	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 191	U	U	U	U	U	U	U	U	U
MDL (95%)	6.2	8.6	5.3	5.9	32.3	4.2	6.7	13.1	48.0
U-undetectable									

Table 2 (continued)

	2,6-DNT	DNB	2,4-DNT	TNT	TNB	4-Amino-DNT	2-Amino-DNT	RDX	Tetryl
Kharga April-03 Serie:3 192	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 194	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 196	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 197	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 198	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 199	U	U	U	U	U	U	U	U	U
Kharga April-03 Serie:3 200	U	U	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 3	U	11.5	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 4	U	U	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 5	U	U	U	U	111	U	U	U	U
Sarajevo May-03 Serie:2 7	U	U	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 9	U	U	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 10	U	U	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 11	U	U	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 12	U	U	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 13	U	17.3	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 16	U	U	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 20	U	U	U	8.1	U	U	U	U	U
Sarajevo May-03 Serie:2 21	U	U	U	U	50.1	U	U	U	U
Sarajevo May-03 Serie:2 23	U	U	U	U	9.2	U	U	U	U
Sarajevo May-03 Serie:2 29	U	U	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 30	U	93.8	U	13.2	U	U	U	U	U
Sarajevo May-03 Serie:2 32	U	U	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 33	U	U	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 35	U	U	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 49	U	U	U	U	U	U	U	U	U
Sarajevo May-03 Serie:2 50	U	U	U	U	U	U	U	U	U
MDL (95%)	6.2	8.6	5.3	5.9	32.3	4.2	6.7	13.1	48.0
U-undetectable									

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The principal degradation byproducts of TNT are 4-A-DNT and 2-A-DNT. Samples that contain one or both of these degradation products when TNT values are also reported increases confidence in the presence of TNT. Samples where low levels of TNT are reported, but 4-A-DNT and 2-A-DNT are absent may be due to levels that are below the MDL. When the sample values become less than about 10 ng/g, uncertainty in the values increases.

The soil chemical residues of explosive signature compounds shown in this set of samples were generally absent; however, several samples showed typical landmine signature chemical presence. Reports describing typical landmine soil chemical residues are limited. Jenkins et al. (2000) have reported this information on many landmine types over several annual seasons. In that effort, values for surface soil residues were typically very low with results frequently below the MDL. Only about 22% of the samples have reported values above the MDL. Median values for TNT were about 4 ng/g, DNT was about 16 to 32 ng/g, and 4-A-DNT and 2-A-DNT were 17 to 44 ng/g.

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