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# GICHD Mine Dog Testing Project – Soil Sample Results #2

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Prepared by
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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 second batch of soils received. This batch contained samples from Kharga, Afghanistan, and Mostar and Sarajevo, Bosnia for samples collected in March 2002.

## Acknowledgements

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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 successful landmine detection.

Quarterly samples are planned for collection in potentially two locations in Afghanistan (Kharga and Gardez) and two locations in Bosnia (Sarejevo 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 was 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 #2 received at Sandia National Laboratories on October 18, 2002. The Swedish Defense Research Establishment (FOI) and the Geneva International Center for Humanitarian Demining (GICHD) collected these samples in Afghanistan and Bosnia in March 2002.

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 2°C. The samples were placed into a freezer at -10°C until sample preparation began on October 24, 2002. A total of 28 samples were received from Kharga, Afghanistan; 27 from Sarejevo, Bosnia; and, 27 from Mostar, Bosnia. One sample had broken in transit (Mostar March02 SER1 #53). Sample analysis procedures were completed by November 19, 2002.

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.. A 0.8 g (± 0. 01 g) aliquot was removed from each vial and placed into a 5 mL amber screw cap vial with care to avoid stones and organic material. Acetonitrile (4 mL) was added by pipetting (± 0.01 mL) to create a 4:1 solvent to soil ratio. A surrogate (3,4-dinitrotoluene, 25 µL aliquot of 10 mg/L) was placed into each extraction vial as a quality control check on extraction efficiency. 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 one (1) µL autoinjection into a split/splitless injector containing a single taper liner (4 mm i.d. x 78 mm long) using a primary and a confirmation column. 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.

Four sets of 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 (MSD),
5 each soil extract samples,
1 each continuing calibration verification (CCV),
10 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, and 75, 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 |
| 2,4,6-Trinitrobenzene | TNB |
| 2,4,6-Trinitrotoluene | TNT |
| Hexahydro-1,3,5-trinitro-s-triazine | RDX |
| 4-Amino-2,6-Dinitrotoluene | 4A-DNT |
| 2-Amino-4,6-Dinitrotoluene | 2A-DNT |
| Tetryl | Tetryl |

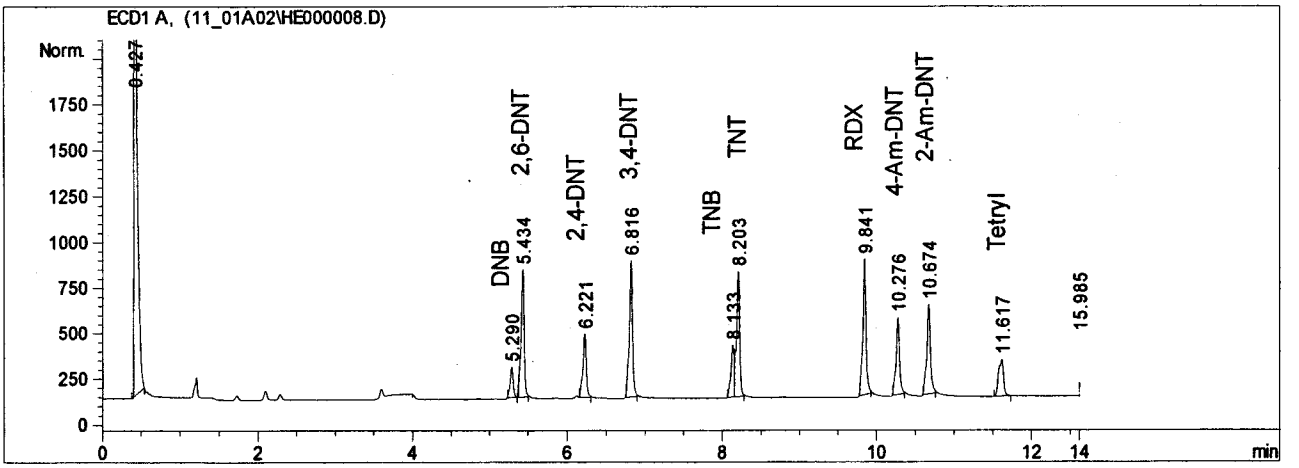


Figure 1. RTX-5 Column Chromatogram - 50 pg standard

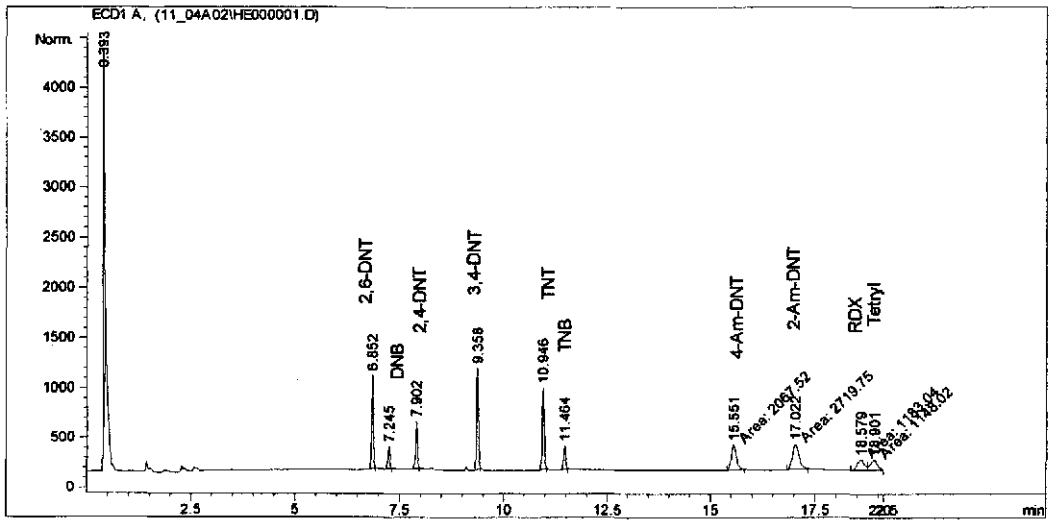


Figure 2. RTX-225 Column Chromatogram – 50 pg standard

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 uses 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 2,4DNT, TNT and RDX on the RTX-5 column in separate sample sets (each in a different LMB sample), but was not confirmed 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, 3 and 4, 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 Tables 2 to 4. As expected, the Tetryl MDL is about ten times greater than for the other analytes. The MDL values shown in Table 2 to 4 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

Tables 2, 3 and 4 show the sample results for the all analytes with acceptable quality control results.

Table 2. Qualified Sample Results – Kharga (ng/g)

| | 1,3-DNB | 2,6-DNT | 2,4-DNT | TNB | TNT | RDX | 4-ADNT | 2-ADNT | Tetryl |
|---|---|---|---|---|---|---|---|---|---|
| kharga mars-02 ser1#1 | U | U | U | U | U | U | U | U | U |
| kharga mars-02 ser1#3 | U | U | U | U | U | U | 29.9 | 40.0 | U |
| kharga mars-02 ser1#5 | U | U | U | U | U | U | U | U | U |
| kharga mars-02 ser1#7 | U | U | U | U | U | U | U | U | U |
| kharga mars-02 ser1#9 | U | U | U | U | U | U | 10.7 | 13.3 | U |
| kharga mars-02 ser1#13 | U | U | U | U | U | U | U | U | U |
| kharga mars-02 ser1#15 | U | U | U | U | U | U | 16.3 | 25.4 | U |
| kharga mars-02 ser1#19 | U | U | U | U | U | U | U | U | U |
| kharga mars-02 ser1#21 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#23 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#25 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#27 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#29 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#31 | U | U | U | U | 11.4 | U | U | U | U |
| Kharga mars-02 ser1#33 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#35 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#37 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#39 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#41 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#43 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#45 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#47 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#49 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#51 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#53 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#55 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#57 | U | U | U | U | U | U | U | U | U |
| Kharga mars-02 ser1#59 | U | U | U | U | 7.9 | U | U | U | U |
| | | | | | | | | | |
| MDL (95% CI) | 8.6 | 6.2 | 5.3 | 32 | 5.5 | 13 | 4.2 | 6.7 | 48 |

U - undetectable

Table 3. Qualified Sample Results – Sarejevo (ng/g)

| | 1,3-DNB | 2,6-DNT | 2,4-DNT | TNB | TNT | RDX | 4-ADNT | 2-ADNT | Tetryl |
|---|---|---|---|---|---|---|---|---|---|
| sarajevo mars-02 ser1#2 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#3 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#5 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#8 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#9 | U | U | 12.3 | U | U | U | U | U | U |
| sarajevo mars-02 ser1#11 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#12 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#16 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#17 | U | U | U | U | 7.2 | U | 11.4 | 15.3 | U |
| sarajevo mars-02 ser1#19 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#20 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#22 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#24 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#26 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#29 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#31 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#32 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#35 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#37 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#39 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#41 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#42 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#45 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#46 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#49 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#50 | U | U | U | U | U | U | U | U | U |
| sarajevo mars-02 ser1#52 | U | U | U | U | U | U | U | U | U |
| | | | | | | | | | |
| MDL (95% CI) | 8.6 | 6.2 | 5.3 | 32 | 5.5 | 13 | 4.2 | 6.7 | 48 |

U - undetectable

Table 4. Qualified Sample Results – Mostar (ng/g)

| | 1,3-DNB | 2,6-DNT | 2,4-DNT | TNB | TNT | RDX | 4-ADNT | 2-ADNT | Tetryl |
|---|---|---|---|---|---|---|---|---|---|
| mostar march-02 ser1#2 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#3 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#6 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#7 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#10 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#11 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#14 | U | U | 10.0 | U | U | U | U | U | U |
| mostar march-02 ser1#15 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#18 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#19 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#22 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#24 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#26 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#27 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#30 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#31 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#34 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#35 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#38 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#39 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#42 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#43 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#45 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#46 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#49 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#50 | U | U | U | U | U | U | U | U | U |
| mostar march-02 ser1#68 | U | U | U | U | U | U | U | U | U |
| | | | | | | | | | |
| MDL (95% CI) | 8.6 | 6.2 | 5.3 | 32 | 5.5 | 13 | 4.2 | 6.7 | 48 |

U - undetectable

The principal degradation byproducts of TNT are 4A-DNT and 2A-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 4ADNT and 2ADNT 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. Values less than the MDL are typically reported as undetectable, but are reported here if also shown on the confirmation column.

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) has 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 10 to 30% of

the samples obtained reported values above the MDL. Median values for TNT were about 4 ng/g, DNT was about 16 to 32 ng/g, and 4A-DNT and 2A-DNT were 17 to 44 ng/g.

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