



**British
Geological Survey**

NATURAL ENVIRONMENT RESEARCH COUNCIL

Analysis of Soil Samples from Kosovo by XRFS and ICP-QMS

DERA Project CU013-0918342

Waste and Pollution Management Programme
Commissioned Report CR/01/264N

BRITISH GEOLOGICAL SURVEY

COMMISSIONED REPORT CR/01/264 N

Analysis of Soil Samples from Kosovo by XRFS and ICP-QMS

DERA Project CU013-0918342

C J B Gowing, S R N Chenery

Contributors

M N Ingham, S J Carter, N D Eatherington, L D Grimsley,
K M Perkins, M A Allen, J R Davis, B Smith.

Key words

XRFS, ICP-QMS, lead, depleted
uranium, isotopes.

Front cover

X-Ray Fluorescence
Spectrometer in the BGS
Analytical Geochemistry
Laboratories.

Bibliographical reference

GOWING, C J B. and Chenery S
R N 2002. Analysis of Soil
Samples from Kosovo by XRFS
and ICP-QMS. *British
Geological Survey
Commissioned Report*,
CR/01/264N. 18 pp.

Contents

1	Introduction.....	1
2	Sample receipt.....	2
2.1	Screening for the presence of asbestos	2
3	Analytical scheme.....	3
3.1	Sample preparation	3
3.2	Determination of Pb and U concentrations by XRFS.....	6
3.2.1	Quality Control in XRFS	6
3.3	Determination of uranium concentrations and uranium isotope ratios by ICP-QMS	7
3.3.1	Quality Control in ICP-QMS.....	8
3.4	Particle size analysis	10
4	Results.....	10
4.1	Comparison of isotope ratio data with published data.....	11
5	References.....	12
	<u>Appendix 1: Analytical methodology</u>	
1	X-Ray Fluorescence Spectrometry	14
2	Inductively Coupled Plasma-Quadrupole Mass Spectrometry	15

Figures

Figure 1.	Schematic flow diagram of the sample preparation route for the first 15 soil samples.	4
Figure 2.	Schematic flow diagram of the sample preparation route for the soil samples with potential asbestos contamination.	5
Figure 3.	Shewhart chart of a QC sample for uranium analysed over a 10 week period.	7

Tables

Table 1.	Sample weights, dose rates and potential of asbestos contamination.....	1
Table 2.	Notified potential of asbestos contamination and results from analysis using polarised light microscopy and dispersion staining techniques.....	2
Table 3.	Sub-samples and excess materials extracted during the sample preparation procedure.	6
Table 4.	Uranium isotope ratios for a synthetic uranium standard with a partial DU signature measured on 14 occasions.....	8
Table 5.	Uranium isotope ratios for geological Reference Material SDO-1 measured on 12 occasions.....	8
Table 6.	Uranium isotope ratios for marine radiological Reference Material IAEA-135.	8
Table 7.	Uranium isotope ratios for geological Reference Material JR-2.	8
Table 8.	Mean and absolute difference in uranium isotope ratios between duplicate pairs of samples (shown in order if increasing $^{238/235}\text{U}$ ratio).	9
Table 9.	Pb and U concentrations determined by XRFS.	10
Table 10.	Uranium isotope ratios determined by ICP-QMS.	11
Table 11.	Uranium isotope ratios from samples believed to have considerable DU signature compared with data from other sources.	12
Table 12.	Instrumental parameters of the Philips PW2400 Wavelength Dispersive-X-Ray Fluorescence Spectrometer.....	14

1 Introduction

A number of soil samples were collected from locations in Kosovo by staff of the then Defence Evaluation and Research Agency (DERA) and since renamed to the Defence Science and Technology Laboratory (DSTL), an agency of the UK Ministry of Defence (MOD). Twenty three samples were collected from DERA, Portsmouth and transported in two aluminium trunks to the British Geological Survey (BGS) on 14 February 2001 for geochemical analysis for the determination of lead and uranium and particle size analysis if significant uranium content was encountered.

All samples had been screened by gamma ray spectrometry at DERA to identify which samples had significant uranium signatures and were thus likely to be contaminated with depleted uranium (DU).

During sampling at one site, Old VJ Barracks, it was noted that a building close to the sampling sites had had an asbestos roof. Consequently, 8 samples were identified as having suspicion of containing asbestos (Table 1).

This report is supplementary to BGS Commissioned Report CR/01/071 (Gowing, 2001a) and CR/01/123 (Gowing, 2001b), which described the first stages of analysis of a number of soil samples by X-Ray Fluorescence Spectrometry for determination of U and Pb content.

Table 1. Sample weights, dose rates and potential of asbestos contamination. The additional sample names shown for information in parentheses are those used in previous reports (Gowing, 2001a and 2001b).

Sample name	Sample weight (g)	Measured dose rate ($\mu\text{Sv/hr}$)	Asbestos risk notified by Client
Slim line soil sample	>3700	<0.1	-
FLY ASH	3000	<0.1	-
G2	2500	<0.1	-
G3	2200	<0.1	-
G4	2900	0.5	-
G5	>3700	0.3	-
H1	>3700	<0.1	-
K1	2800	0.2	-
K2	>3700	0.2	-
ST1	>3700	0.2	-
T1	3600	0.2	-
T2	3000	0.1	-
W1	3100	<0.1	-
W2	>3700	0.2	-
W3	3400	0.3	-
1A (1 not adj)	300	<0.1	caution required
3A	1100	0.5	likely to contain asbestos
3B (3ADJ)	650	1.2	likely to contain asbestos
4A	450	0.5	likely to contain asbestos
4B	>3700	0.5	likely to contain asbestos
5A	2900	0.2	caution required
5B	>3700	<0.1	caution required
2 (61/01 3)	60	2.2	caution required

2 Sample receipt

On receipt at BGS, the sealed aluminium trunks were placed in the radiochemical laboratory, a radiological supervised area. The external dose rates were monitored using a mini-monitor type 900/44a before the trunks were opened and the sample containers extracted. Most samples were doubled bagged in polythene bags and sample 2 was in a plastic tub.

The external dose rate of each of the samples was measured through its sample container. Measured dose rates are presented in Table 1, from which it can be seen that the inherent radiological hazard exceeded BGS working guidelines ($<2 \mu\text{Sv/hr}$) for only one sample. The relatively enhanced dose rate measured in some samples is probably due to caesium (in G4, 4A and 4B) and uranium (in 3A, 3B and 2) identified by the gamma ray spectrometry.

The samples were then registered into the BGS Analytical Geochemistry Laboratories' quality system as Laboratory Number 06919.

2.1 Screening for the presence of asbestos

Eight samples were identified as having suspicion of containing asbestos, in varying amounts from 'likely' to 'caution required' (Table 1). The 8 samples were then removed from BGS by DERA staff. Sub-samples of 6 of these 8 samples were sent to the Atomic Weapons Establishment (AWE) at Aldermaston for screening for the presence of asbestos. Staff at AWE first screened the samples by gamma spectrometry analysis to see whether they were safe to handle from a radiological perspective.

AWE reported that samples 3A and 3B could not be analysed for asbestos "because of the levels of DU present". The remaining samples (4A, 4B, 5A and 5B) were then analysed "using polarised light microscopy and dispersion staining techniques in accordance with HSE standard method MDSHS 77". All 4 samples were reported to have "No asbestos found". The results are shown in Table 2.

Table 2. Notified potential of asbestos contamination and results from analysis using polarised light microscopy and dispersion staining techniques.

Sample name	Asbestos risk notified by Client	Screening results from AWE, Aldermaston	Screening results from BGS
1A	caution required	-	No asbestos found
3A	likely to contain asbestos	Could not be analysed	No asbestos found
3B	likely to contain asbestos	Could not be analysed	No asbestos found
4A	likely to contain asbestos	No asbestos found	-
4B	likely to contain asbestos	No asbestos found	-
5A	caution required	No asbestos found	-
5B	caution required	No asbestos found	-
2	caution required	-	No asbestos found

The eight samples were returned to BGS from AWE sealed in two metal tins: container A housed samples 1A and 2 and container B housed samples 3A, 3B, 4A,

4B, 5A and 5B. The external dose rates of the tins were monitored using a mini-monitor type 900/44a before the containers were opened and found to be <1 $\mu\text{Sv/hr}$.

After an extensive risk assessment covering the handling of materials that may have both DU and asbestos contamination, the remaining four samples (1A, 3A, 3B and 2) were screened for the presence of asbestos as part of further investigation (Milodowski 2001a and 2001b) using scanning electron microscopy (SEM). The absence of asbestos is detailed in Table 2.

3 Analytical scheme

The BGS Analytical Geochemistry Laboratories were formally awarded accreditation by the United Kingdom Accreditation Service (UKAS) on 16 August 1999 and are UKAS accredited testing laboratory number 1816. The Analytical Geochemistry UKAS Procedures constitute Section AGN of the BGS Quality System Manual, which itself conforms to the requirements of BS EN ISO 9001:1994; this is presently being revised to be in line with the new ISO 9001:2000 standard. All activities in the Laboratories are subject to regular internal audits.

The 15 samples that were not potentially contaminated with asbestos were prepared according to the sample preparation route shown in Figure 1, which ensured that the sample taken for analysis was representative of the original material. A slightly amended route (Figure 2) was followed for the 8 samples removed by DERA staff, as the original samples had been sub-sampled. The route used for these samples ensured that the analytical sample was representative of the split received after the screening for asbestos.

In both cases the final stages of the sample preparation were to take a sub-sample for analysis by for subsequent Inductively Coupled Plasma-Quadrupole Mass Spectrometry (ICP-QMS) and to press a pellet, for analysis by X-Ray Fluorescence Spectrometry (XRFS).

3.1 Sample preparation

Before starting any preparation work a risk assessment was carried out covering the handling of potentially radioactively contaminated samples; guidance in completing this assessment was taken from the BGS radiation protection adviser, the National Radiological Protection Board.

The samples were prepared for analysis following a route outlined in Figure 1 or Figure 2. At each stage any excess material was carefully bagged and labelled. Sub-samples and excess portions extracted during the sample preparation procedure are catalogued in Table 3.

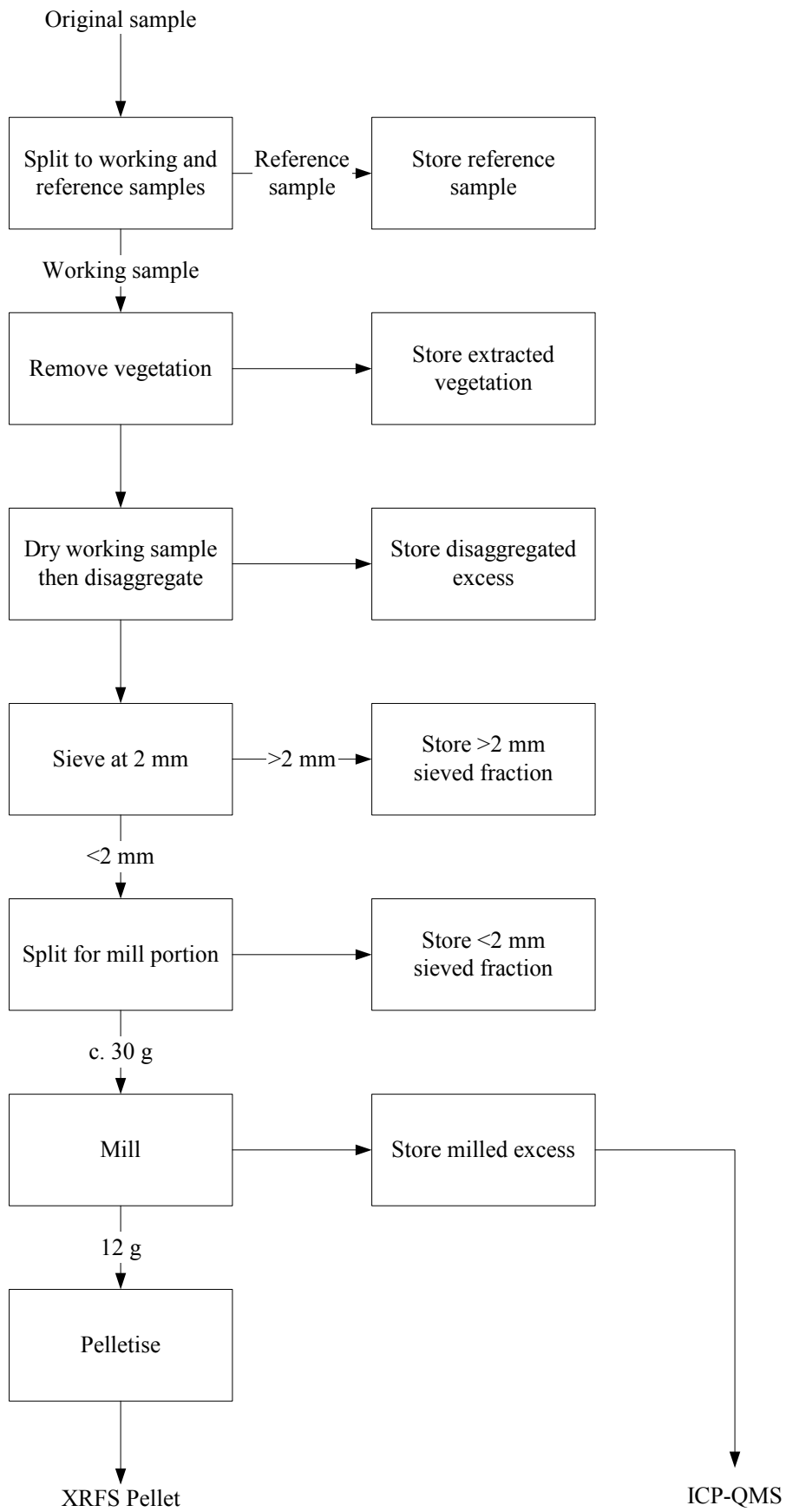


Figure 1. Schematic flow diagram of the sample preparation route for the first 15 soil samples.

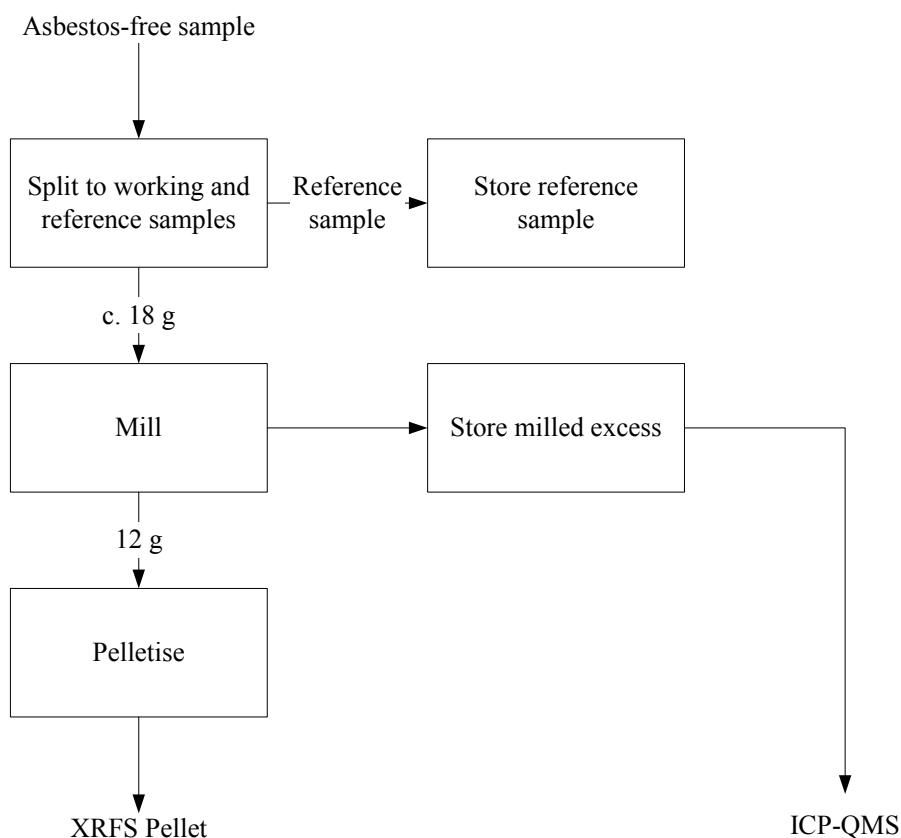


Figure 2. Schematic flow diagram of the sample preparation route for the soil samples with potential asbestos contamination.

Each of the first 15 samples was first split by cone quartering to give a reference sample, for further or corroborative work and particle size analysis, if required. Any large pieces of vegetation were then removed so that all samples were comparable. The working sample was then dried at 35°C at least overnight and disaggregated using a porcelain pestle and mortar. A portion of the disaggregated sample was then sieved on a 2 mm nylon mesh to remove the coarse fraction of the soil. A sub-sample of the <2 mm sieved fraction was then taken and milled in an agate ball mill for 30 minutes to reduce particle size to 99% $\leq 50 \mu\text{m}$.

Analytical sub-samples (c. 18 g) of the remaining 8 samples were taken by coning and spot sampling over the cone. This material was milled in an agate ball mill for 20 minutes to reduce particle size to 99% $\leq 50 \mu\text{m}$.

An aliquot of 12 g of the milled material from each sample was then mixed thoroughly with 3 g of a wax binder (a mixture of 9 parts EMU120FD styrene copolymer (BASF plc) and 1 part Ceridust 3620 micronised polyethylene wax (Hoechst), after Van Zyl (1982)) for 3 min in the agate ball mill. This mixture was then pressed into a 40 mm diameter pellet at 25 t load applied for 4 s. Excess material from the milling stage was retained for further work either for an additional XRF pellet or for analysis by another method, e.g. ICP-QMS.

Table 3. Sub-samples and excess materials extracted during the sample preparation procedure. The last 8 rows describe sub-samples of the samples removed by DERA staff for asbestos screening.

Sample name	Reference sample	Vegetation	Disagg. excess	>2 mm portion	<2 mm excess	Milled excess	Pellet
Slim line soil sample	x		x	x	x	x	x
FLY ASH	x		x	x	x	x	x
G2	x		x	x	x	x	x
G3	x		x	x	x	x	x
G4	x		x	x	x	x	x
G5	x		x	x	x	x	x
H1	x		x	x	x	x	x
K1	x	x	x	x	x	x	x
K2	x		x	x	x	x	x
ST1	x		x	x	x	x	x
T1	x		x	x	x	x	x
T2	x		x	x	x	x	x
W1	x		x	x	x	x	x
W2	x		x	x	x	x	x
W3	x	x	x	x	x	x	x
1A	x					x	x
3A	x					x	x
3B	x					x	x
4A	x					x	x
4B	x					x	x
5A	x					x	x
5B	x					x	x
2	x					x	x

3.2 Determination of Pb and U concentrations by XRFS

Analysis of stream-sediment and soil samples for determination of major and trace elements is routinely carried out for a number of projects, including the Geochemical Baseline Survey of the Environment (British Geological Survey, 1997 and 2000) at BGS, by both energy dispersive (ED) and wavelength dispersive (WD) XRFS (Ingham and Vrebos, 1994).

Uranium was determined on a bespoke calibration optimised for the determination of this element. The calibration and validation are documented by Ingham and Gowing (in prep.). Lead was determined in the first 15 samples using the routine BGS method for determination of heavy metals and in the following 8 samples by a similar calibration incorporated within the calibration used for the determination of uranium.

The optimised uranium calibration method had to be re-calibrated after analysis of the first 15 samples and before analysis of the final 8 samples owing to the time taken to assess the potential asbestos contamination and an instrument breakdown. The second calibration was validated in the same way as the first (Ingham and Gowing, in prep.). A brief description of the principles of XRFS is given in Appendix 1.

3.2.1 Quality Control in XRFS

Routine laboratory Quality Control (QC) was monitored by daily analysis of 2 QC samples. Data from these analyses were plotted on Shewhart charts using a QC package (QI Analyst) to identify discrepant analytical runs or undue instrumental

drift. Any suites of samples governed by a failing QC sample were re-analysed. One of the Shewhart charts, shown in Figure 3, demonstrates the reproducibility of the uranium calibration over 10 weeks; a mean of 30.2 ppm and standard deviation of 0.35 ppm give a relative standard deviation of 1.2%.

Data are stored on a local PC during analysis and then collated into a spreadsheet (Microsoft Excel) prior to reporting. Spreadsheets are stored at BGS on a server that is regularly backed up.

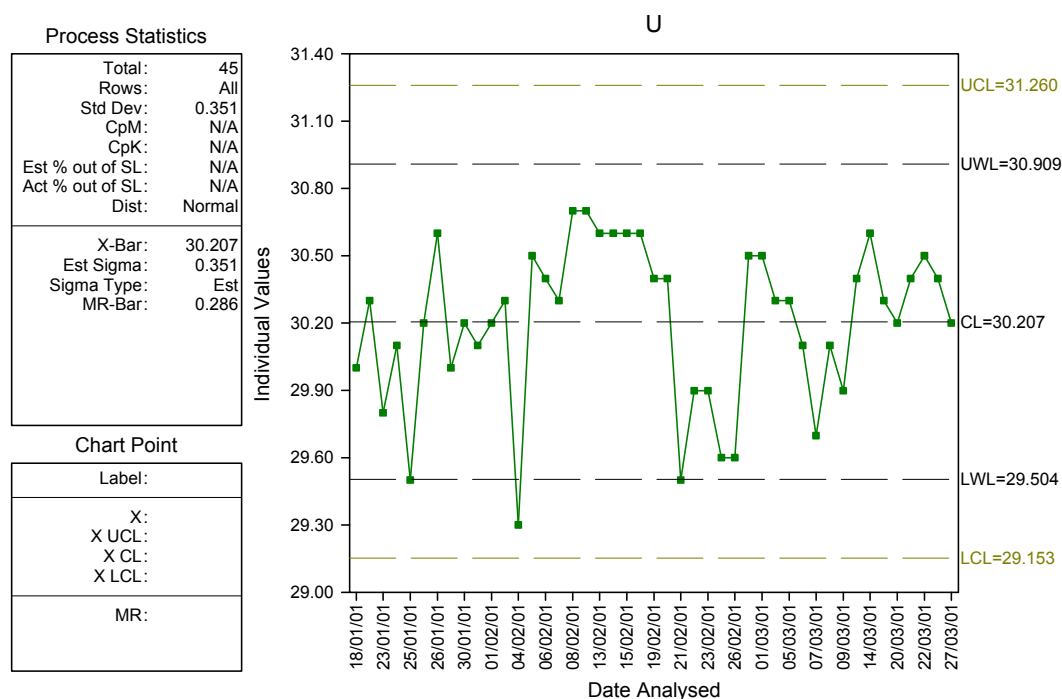


Figure 3. Shewhart chart of a QC sample for uranium analysed over a 10 week period. Upper (U) and Lower (L) Control Limits (CL) and Warning Limits (WL) are shown at mean \pm 3 standard deviations (CL) and mean \pm 2 standard deviations (WL).

3.3 Determination of uranium concentrations and uranium isotope ratios by ICP-QMS

The uranium isotope ratios $^{238/234}\text{U}$ and $^{238/235}\text{U}$ were measured by ICP-QMS as part of an investigation into the dissemination of depleted uranium into the environment. The following analytical procedure was used for these analyses: (i) dissolution of the ground solid samples using a mixed acid attack; (ii) determination of uranium concentrations in those samples by ICP-QMS; (iii) separation and pre-concentration of uranium from other matrix elements; (iv) determination of uranium isotope ratios under optimal ICP-QMS conditions. The reagents, equipment and methods are described in detail in Appendix 1.

The results of the most DU contaminated materials were then compared to recently published values for penetrator samples as an indication of analytical quality, including the possibility of determining $^{238/236}\text{U}$ isotope ratios as a positive indicator of the presence of DU.

3.3.1 Quality Control in ICP-QMS

Between and within run reproducibility was monitored using data from a geological Reference Material (SDO-1) and a synthetic uranium standard described in Appendix 1. Accuracy was monitored by comparison of data from Reference Materials IAEA-135 and JR-2 with literature/certificate values. QC data for the sample dissolution/analytical runs are summarised in Tables 4-7 then discussed so that the sample results may be considered in the analytical context.

Table 4. Uranium isotope ratios for a synthetic uranium standard with a partial DU signature measured on 14 occasions.

Synthetic standard	$^{238/234}\text{U}$	$^{238/235}\text{U}$
Mean	46157	301
Standard deviation	918	1.0
RSD (%)	2.0	0.3

Table 5. Uranium isotope ratios for geological Reference Material SDO-1 measured on 12 occasions.

SDO-1	$^{238/234}\text{U}$	$^{238/235}\text{U}$
Mean	18090	137.9
Standard deviation	257	0.13
RSD (%)	1.4	0.09

Table 6. Uranium isotope ratios for marine radiological Reference Material IAEA-135.

IAEA-135	Mean $^{238/234}\text{U}$	2sem $^{238/234}\text{U}$	Mean $^{238/235}\text{U}$	2sem $^{238/235}\text{U}$
IAEA-135 duplicate A	19220	432	137.7	0.3
IAEA-135 duplicate B	19256	392	137.7	0.3
Expected	19876	5091	184.0	64

Table 7. Uranium isotope ratios for geological Reference Material JR-2.

JR-2	Mean $^{238/234}\text{U}$	2sem $^{238/234}\text{U}$	Mean $^{238/235}\text{U}$	2sem $^{238/235}\text{U}$
JR-2 this work	17997	414	138.2	0.3
Expected ¹	18225		137.9*	

¹Yokoyama *et al.* (2001). * Natural sample

It may be observed from Tables 4 and 5 that the precision of the $^{238/234}\text{U}$ and the $^{238/235}\text{U}$ ratios are better for the SDO-1 reference material than the synthetic standard. This is the result of the better counting statistics associated with the high proportions of ^{234}U and ^{235}U .

To test the accuracy of the method, two other Reference Materials were analysed: IAEA-135, which has been certified for uranium isotopes (Table 6), and JR-2 (Table 7). The agreement with the certified values for $^{238/234}\text{U}$ is very good and within error (IAEA ratios and errors propagated from data sheet). However, the agreement for the $^{238/235}\text{U}$ is much poorer, although still within error. This is probably due to the poor quality of the reference data reported on the data sheet. Presumably, these are relatively old data and obtained by radiometric counting, which can be

particularly poor for ^{235}U . However, the agreement with the recently published data (determined using thermal ionisation mass spectrometry, the benchmark technique) on reference material JR-2 is extremely good (Yokoyama *et al.*, 2001) and well within error for both ratios.

A further measure of reproducibility of the analytical technique that takes into account the sample matrix is the analysis of duplicate pairs of samples. Table 8 contains information derived from these pairs. If the precision of analysis was solely a function of the counting statistics, we would expect the absolute difference to increase randomly with increasing isotope ratio and be similar in magnitude to that observed above with reference materials/synthetic standard. However, this is not so. The smallest differences between duplicate pairs occur when the samples have either a completely natural signature or a completely DU signature.

This observation can be readily explained by a ‘nugget’ effect. The isotope signature of a sample with completely natural or completely depleted uranium is the same, whether the uranium is highly concentrated in small grains or evenly distributed throughout the sample. However, if a sample contains homogeneously distributed natural uranium but depleted uranium in a few small nuggets, then replicate samples may contain different numbers of nuggets and hence may have significantly different ratios. This is apparent in the duplicate analyses shown in Table 8 particularly for samples 4B, 4A, 5A and 3A.

This conclusion is supported by the scanning electron microscopy observations on samples 1A, 2, 3A and 3B (Milodowski, 2001a and 2001b) which show that the metallic and oxidised metallic DU occurs as discrete particles on the surface of soil fragments and not uniformly distributed throughout the sample matrix.

Table 8. Mean and absolute difference in uranium isotope ratios between duplicate pairs of samples (shown in order of increasing $^{238/235}\text{U}$ ratio).

Sample name	$^{238/235}\text{U}$	$^{238/235}\text{U}$	$^{238/234}\text{U}$	$^{238/234}\text{U}$
	Mean	Difference	Mean	Difference
W1	137.68	0.1	19282	199
G3	137.75	0.4	17662	347
K1	137.76	0.04	18531	111
T2	137.81	0.02	19860	192
T1	137.82	0.1	18804	364
G4	138.02	0.3	17962	249
4B	140.50	0.9	18537	182
5B	141.18	0.2	18300	568
4A	145.22	8.3	19499	1320
5A	153.81	4.9	20842	1095
3A	489.43	2.1	137671	3460
3B	493.42	0.4	137475	9509
2	497.36	0.7	142284	9325

The duplicate sample data can be used further to calculate the overall precision of the analytical measurements across all the samples, including the sampling errors associated with ‘nugget’ effects. This is carried out by performing analysis of variance (ANOVA), the results of which give a standard deviation value of 1.9 for $^{238/235}\text{U}$ and 2725 for $^{238/234}\text{U}$. Therefore, we may expect our results to have a variation approximately 4 for $^{238/235}\text{U}$ and approximately 6000 for $^{238/234}\text{U}$.

3.4 Particle size analysis

Although none of the 15 samples first analysed had sufficient uranium concentration to warrant investigation by particle size analysis, detailed investigations of samples 1A, 3A, 3B and 2 have been undertaken using scanning electron microscopy. These investigations are the subjects of two separate BGS reports: CR/01/145 for samples 1A and 2 (Milodowski, 2001a) and CR/01/261 for samples 3A and 3B (Milodowski, 2001b).

4 Results

The fully validated results for Pb and U concentrations determined by XRFS are shown in Table 9. The lower limit of detection for both Pb and U using this calibration is 1 ppm. This is a theoretical value for the concentration equivalent to three standard deviations above the background count rate for the analyte in a silica matrix. High instrumental stability results in practical values for these materials approaching the theoretical.

Table 9. Pb and U concentrations determined by XRFS.

Sample name	Pb ppm	U ppm
Slim line soil sample	205	3
FLY ASH	13	3
G2	128	3
G3	93	3
G4	78	3
G5	59	3
H1	49	3
K1	88	5
K2	70	4
ST1	49	3
T1	57	3
T2	67	4
W1	52	4
W2	50	4
W3	51	4
1A	21	6
3A	165	149
3B	52	983
4A	64	3
4B	57	3
5A	65	3
5B	58	2
2	31	1430

The fully validated results of the uranium isotope determinations on the samples are shown in Table 10.

Table 10. Uranium isotope ratios determined by ICP-QMS. Replicate determinations using the full procedure were made for some samples and are sub-coded A and B. 2sem (2 x standard error of the mean) was calculated from the standard deviation of 50 measured ratios of the individual sample solution and is a measure of the internal precision of the measurement and equivalent to 95% confidence limits of the mean of the 50 ratios.

Sample Name	BGS ID No	Isotope ratio $^{238/235}\text{U}$	2sem $^{238/235}\text{U}$	Isotope ratio $^{238/234}\text{U}$	2sem $^{238/234}\text{U}$
<i>Natural Expected Ratio</i>		<i>137.9</i>		<i>18116</i>	
Slim line soil sample	06919-0001	138.3	0.3	18309	366
FLY ASH	06919-0002	138.3	0.3	17205	380
G2	06919-0003	138.3	0.3	17676	442
G3	06919-0004A	137.9	0.3	17835	429
G3	06919-0004B	137.6	0.3	17489	474
G4	06919-0005A	137.9	0.3	17837	415
G4	06919-0005B	138.2	0.2	18086	414
G5	06919-0006	137.5	0.2	18473	343
H1	06919-0007	137.7	0.2	20951	467
K1	06919-0008A	137.8	0.3	18586	374
K1	06919-0008B	137.7	0.2	18475	434
K2	06919-0009	137.9	0.3	18858	461
ST1	06919-0010	137.6	0.3	17573	383
T1	06919-0011A	137.9	0.2	18985	372
T1	06919-0011B	137.8	0.2	18622	380
T2	06919-0012A	137.8	0.3	19764	400
T2	06919-0012B	137.8	0.3	19956	420
W1	06919-0013A	137.7	0.3	19183	355
W1	06919-0013B	137.6	0.2	19381	389
W2	06919-0014	137.4	0.3	18937	424
W3	06919-0015	137.4	0.3	18526	394
1A	06919-0016	278.3	0.7	47491	1935
3A	06919-0017A	488.4	2.6	135941	10279
3A	06919-0017B	490.5	2.2	139400	12061
3B	06919-0018A	493.6	1.6	132720	8701
3B	06919-0018B	493.2	2.1	142230	11514
4A	06919-0019A	141.1	0.2	18839	327
4A	06919-0019B	149.4	0.3	20159	519
4B	06919-0020A	140.1	0.2	18446	345
4B	06919-0020B	140.9	0.3	18628	449
5A	06919-0021A	156.2	0.3	21390	497
5A	06919-0021B	151.4	0.3	20294	361
5B	06919-0022A	141.1	0.2	18016	468
5B	06919-0022B	141.3	0.3	18584	371
2	06919-0023A	497.7	2.3	137622	9586
2	06919-0023B	497.0	2.0	146946	13627

4.1 Comparison of isotope ratio data with published data

Data on uranium isotope ratios from penetrators fired in the Balkans has recently been published by Boulyga *et al.* (2001). Data for samples that were believed to have an almost complete DU signature (1A, 3A, 3B, and 2) are compared with data from Boulyga *et al.* (2001) and DU data recently provided to the analysts by B Smith, BGS (*pers. comm.*) in Table 11.

Table 11. Uranium isotope ratios from samples believed to have considerable DU signature compared with data from other sources.

Sample name	Mean $^{238/234}\text{U}$	2sem $^{238/234}\text{U}$	Mean $^{238/235}\text{U}$	2sem $^{238/235}\text{U}$	Mean $^{238/236}\text{U}$	2sem $^{238/236}\text{U}$
Natural Expected	18116	-	137.9	-	none	-
1A	47491	1935	278.3	0.7	51259	2326
3A duplicate A	135941	10279	488.4	2.6	33623	1203
3A duplicate B	139400	12061	490.5	2.2	33514	1381
3B duplicate A	132720	8701	493.6	1.6	33445	1115
3B duplicate B	142230	11514	493.2	2.1	33182	960
2 duplicate A	137622	9586	497.7	2.3	33252	1210
2 duplicate B	146946	13627	497.0	2.0	32418	938
Penetrator sample ¹	125000	7353	495.0	2.4	32258	3687
DU Reprocessed ²	56942	-	284.7	-	-	-
DU from tailings ²	142570	-	499.0	-	-	-
DU used at Kircudbright ²	121204	-	-	-	-	-

¹ Boulyga *et al.*, 2001. ² Smith (*pers. comm.*).

As the data from Boulyga *et al.* (2001) suggested that there was a significant content of ^{236}U in DU, it was decided to measure this ratio as well in the final batch of 4 samples (1A, 3A, 3B and 2). The agreement with the Boulyga *et al.* (2001) data is within error for all 3 ratios and particularly good for $^{238/235}\text{U}$ and $^{238/236}\text{U}$. As ^{236}U does not effectively exist naturally this is a good marker for DU and it is proposed to measure this ratio regularly in future.

5 References

Boulyga, S F, Testa, C, Desideri, D and Sabine Becker, J (2001). Optimisation and application of ICP-MS and alpha spectrometry for the determination of isotopic ratios of depleted uranium and plutonium in samples collected in Kosovo. *J. Anal. At. Spectrom.*, **16**, 1283-1289.

British Geological Survey (1997). Regional geochemistry of parts of North-west England and North Wales. British Geological Survey, Keyworth, Nottingham.

British Geological Survey (2000). Regional Geochemistry of Wales and parts of west-central England: stream sediment and soil. British Geological Survey, Keyworth, Nottingham.

Gowing, C J B (2001a). Analysis of Soil Samples from Kosovo. British Geological Survey Commissioned Report, CR/01/071, 10 pp.

Gowing, C J B (2001b). Analysis of Soil Samples from Kosovo. British Geological Survey Commissioned Report, CR/01/123, 6 pp.

Ingham, M N and Gowing, C J B (in prep.). Validation Report. The Determination of Uranium and Lead by X-ray Fluorescence Spectrometry. British Geological Survey, Keyworth, Nottingham.

Ingham, M N and Vrebos, B A R (1994). High Productivity Geochemical XRF Analysis. *Advances in X-ray Analysis*, **37**, 717-724.

Milodowski, A E (2001a). A trial investigation by scanning electron microscopy of uranium particulate in building debris associated with a Depleted Uranium munitions strike site during the Kosovo Conflict. British Geological Survey Commissioned Report, CR/01/145, 20 pp.

Milodowski, A E (2001b). Scanning electron microscopy of uranium particulate in two soil samples at a Depleted Uranium munitions strike site from the Kosovo Conflict. British Geological Survey Commissioned Report, CR/01/261, 11 pp.

Smith, B (*Pers. Comm.*).

Van Zyl, C (1982). Rapid preparation of robust pressed powder briquettes containing a styrene and wax mixture as a binder. *X-ray Spectrometry*, **11** (1), 29-31.

Yokoyama, T, Makishima, A and Nakamura, E (2001). Precise analysis of $^{234}\text{U}/^{238}\text{U}$ ratio using UO_2^+ ion with thermal ionization mass spectrometry for natural samples. *Chem. Geol.*, **181**, 1-12.

Appendix 1: Analytical methodology

1 X-Ray Fluorescence Spectrometry

Pellets were analysed by Wavelength Dispersive-X-Ray Fluorescence Spectrometry (WD-XRFS) using a Philips PW2400 spectrometer fitted with a 102 position sample changer and a 3 kW/60 kV rhodium anode x-ray tube and controlled by Philips SuperQ software. The full configuration of the instrument is given in Table 12.

Table 12. Instrumental parameters of the Philips PW2400 Wavelength Dispersive-X-Ray Fluorescence Spectrometer.

Model:	PW2400		
Serial No:	DY611		
Tube:	Rhodium Super Sharp Tube		
Tube rating:	3 kW		
	Max. 60 kV		
	Max. 125 mA		
Detectors:	Gas Flow Proportional Counter (2 μm window)		
	Scintillation Counter		
Gas:	Argon/Methane (P10)		
Crystals/ 2d spacing \AA :	LiF220	2.848	(lithium fluoride)
	LiF200	4.027	(lithium fluoride)
	GE111	6.532	(germanium)
	PE002	8.742	(pentaerythritol)
	PX-1	49.1	(multi-layer)
Beam filters/ Thickness	Brass	100 μm	
	Brass	300 μm	
	Aluminium	200 μm	
	Aluminium	750 μm	
Channel masks (diameters):	48 mm		
	37 mm		
	25 mm		
	30 mm		
Collimator spacing:	700 μm		
	300 μm		
	100 μm		
Sample Changer:	PW2510 102 positions		

In WD-XRFS, the sample pellet is irradiated by x-rays, which in turn cause secondary x-ray fluorescence of the atoms within the sample. This secondary radiation is collimated onto a diffraction crystal and its intensity at selected peak and background positions in the x-ray spectrum is measured using a detector mounted onto a goniometer. The net intensity at each of the peak positions is calibrated against known synthetic standards and Reference Materials.

The calibrations are validated by analysis of Reference Materials. Instrumental drift is corrected for twice weekly. Corrections are made within the calibrations for matrix

effects and spectral line overlap interferences. Inherent mineralogical and particle size effects contribute to the overall analytical error.

2 Inductively Coupled Plasma-Quadrupole Mass Spectrometry

2.1 Procedure for the dissolution of solid materials

2.1.1 Reagents and equipment

Concentrated hydrofluoric acid (HF) – Aristar[®] grade
Concentrated nitric acid (HNO₃) – Aristar[®] grade
Concentrated perchloric acid (HClO₄) – Aristar[®] grade
10% v/v HNO₃ in 18 MΩ quality water – Aristar[®] grade
PTFE test tubes – 100 mm long, 15 mm i.d.
BPL s.t.a.t.u.s. programmable hot block

2.1.2 Method

Dissolution of the ground sample material was performed as follows. A sample mass of 0.1g was accurately weighed into PTFE tubes. 1 ml conc. HF, 0.8 ml conc. HNO₃ and 0.4 ml conc. HClO₄ acid were added and the PTFE tube heated to dryness in a programmable hot block over 12 hours. The residual digested sample was re-dissolved in 5 ml of 10% v/v HNO₃ and stored in high density polyethylene (HDPE) bottles prior to use.

Quality control (QC) samples included blanks, duplicate samples and the geochemical Reference Materials SDO-1 (a shale from United States Geological Survey), JR-2 (a rhyolite from Japanese Geological Survey) and IAEA-135 (a marine sediment from International Atomic Energy Authority).

2.2 Procedure for the determination of uranium concentrations

2.2.1 Reagents and equipment

10% v/v HNO₃ in 18 MΩ quality water – Aristar[®] grade
1% v/v HNO₃ in 18 MΩ quality water – Aristar[®] grade
Calibration solutions - 2, 10, 50 ng ml⁻¹ diluted by volume, with 1% HNO₃, from “Multi-Element Solution 2”, Claritas PPT[™], Spex CertiPrep Inc., Metuchen, N.J., USA.
QC solutions – 10 ng ml⁻¹ diluted by volume, with 1% HNO₃, from “ICP-MSCS”, High Purity Standards, Charleston, SC, USA.
Internal standard solutions - 20 ng ml⁻¹ diluted by volume, with 1% HNO₃, from “In single element standard” and “Bi single element standard”, Claritas PPT[™], Spex CertiPrep Inc., Metuchen, N.J., USA.
VG Elemental (now ThermoElemental) PQ ExCell ICP-QMS.

2.2.2 Method

The dissolved samples were further diluted on the day of analysis using 1% HNO₃ and internal standard elements indium and bismuth added at a concentration of

10 ng ml⁻¹, to give a final dilution factor of 1000. The ICP-QMS instrument was calibrated with commercial certified chemical standards, over the concentration range 0-50 ng ml⁻¹. Samples that exceeded the calibration range were further diluted and re-analysed. The QC samples were added periodically throughout the analytical run to monitor the calibration performance, including blanks, duplicate samples and the geochemical Reference Materials SDO-1, JR-2 and IAEA-135.

2.3 Uranium matrix separation and pre-concentration procedure

2.3.1 Rational

The precision of the isotopic ratio measurements is limited by counting statistics for the ²³⁴U⁺ and ²³⁵U⁺ ions, therefore it was preferable to make the measurement at the maximum concentration of uranium within the limits of ICP-QMS detector linearity (²³⁸U⁺ count rate of 2 Mcps). The typical sensitivity of the BGS PQ ExCell instrument is 50 Mcps/ppm. Thus, the optimal target concentration of sample solutions was calculated as 20 ppb (ng ml⁻¹) equivalent to 1 Mcps, allowing a safety margin factor of 2.

The minimum volume of sample required for analysis was 10 ml; therefore an absolute uranium mass of 200 ng (i.e. 20 ng ml⁻¹) needed to be separated using the ion-exchange column. The volume of digested sample to be passed through the column was then individually calculated from the sample total uranium concentration determined.

2.3.2 Reagents and equipment

10% v/v HNO₃ in 18 MΩ quality water – Aristar[®] grade

0.025M ammonium oxalate – AnalaR[®] grade in 0.1% v/v HNO₃

0.1% v/v HNO₃ in 18 MΩ quality water – Aristar[®] grade

Pre-packed Tru-Spec Ion Exchange Column containing 2 ml of resin, Eichrom Europe, Paris, France.

2.3.3 Method

1. Drain storage acid to waste.
2. Add 4 ml of 0.025M ammonium oxalate in 0.1% HNO₃ and drain to waste. *Blanking phase.*
3. Add 4 ml of 0.1% HNO₃ and drain to waste. *Washing phase.*
4. Add 2 ml of 10% HNO₃ and drain to waste. *Column conditioning phase.*
5. Add 2 ml or more of sample in 10% HNO₃ and drain to waste. *Sample loading phase.*
6. Add 2 ml of 10% HNO₃ and drain to waste. *Sample wash-in phase.*
7. Add 4 ml of 0.1% HNO₃ and drain to waste. *Major element wash-out phase.*
8. Add 4 ml of 0.025M ammonium oxalate in 0.1% HNO₃ and collect in appropriate container until needed for analysis. *Uranium collection phase.*
9. Add 4 ml of 0.025M ammonium oxalate in 0.1% HNO₃ and drain to waste. *Blanking phase.*

10. Add 4 ml of 0.1% HNO₃ and drain to waste. *Washing phase.*

11. Add 2 ml of 0.1% HNO₃ and immediately cap column top and bottom. *Wet Storage.*

2.4 Determination of uranium isotope ratios

2.4.1 Reagents and equipment

1% v/v HNO₃ in 18 MΩ quality water – Aristar[®] grade

QC solutions – 15 ng ml⁻¹ U diluted by volume, with 1% HNO₃, from single element solution, Aldrich Chemical Co.

VG Elemental (now ThermoElemental) PQ ExCell ICP-QMS

2.4.2 ICP-QMS optimisation for uranium isotope work

All isotope measurements were made on the BGS VG PQ ExCell instrument. To ensure these were optimised, the signal of the ²³⁸U⁺ ion was maximised within the linear range of the detector system.

Firstly the instrument gas flows and ion lenses were tuned for maximum sensitivity of the ²³⁸U⁺ ion (approx. 50 Mcps/ppm). For the isotope measurements, only the pulse counting mode was used. The pulse counting mode is linear to 2 million counts providing the dead-time correction of the detector is accurately applied. Therefore the second part of the optimisation was to establish the correct dead time for uranium. To achieve this, a series of uranium solutions of different concentrations close to the linear limit were analysed with different dead-time correction values and the ^{238/235}U isotope ratios compared. At the correct dead-time correction value the isotope ratio will be constant despite changes in concentration. The dead-time was checked before every analytical run and a typical value was 40 ns.

The third parameter optimised was dwell time. This is the time the mass spectrometer sits at a particular mass position acquiring data. There are a number of competing factors limiting its choice for each isotope: (i) relative abundance of the isotope, i.e. counting statistics; (ii) time for the quadrupole to jump to a new mass position and settle; and (iii) noise sources in the plasma. To minimise (iii) the settle time was made as short as possible until data was limited by (i) and (ii). A dwell time of 2.5 ms for ²³⁴U⁺, ²³⁵U⁺ and ²³⁸U⁺ was chosen. During the last analytical run, where the DU component was expected to be a high proportion of the total uranium, the ²³⁶U isotope was also measured with a dwell time of 2.5 ms.

2.4.3 Determination of uranium isotope ratios ^{238/235}U and ^{238/234}U

On the day of analysis, aliquots of the separated uranium samples were diluted to give 10 ml of solution with a uranium concentration chosen to give an ICP-QMS response of 1 Mcps for ²³⁸U.

To correct for instrumental mass bias, the natural rock reference material SDO-1, which will have the fixed natural ^{238/235}U ratio, was analysed periodically throughout the analytical runs. This bias is the result of an inherent systematic change in instrument sensitivity with mass and is known to vary with time and cone blockage. To monitor this correction, a synthetic uranium standard with a partial DU component (^{238/235}U approximately 300) was run as a QC sample every 10 samples.

Individual standard and sample data were acquired using an auto-sampler using the following procedure: 2 minutes uptake and stabilisation; 50 integrations, each of 10 seconds duration; 2 minute wash with 2% HNO₃. The instrument software was used to calculate the measured isotope ratios from the raw isotope responses and to calculate a mean and standard deviation for those 50 measured ratios.

Data were then exported to a Microsoft Excel spreadsheet for further processing in the following manner: (i) digestion blanks were checked and not found to be significant; (ii) ^{238/235}U isotope ratios were normalised to the first SDO-1 reference material and by interpolation between subsequent SDO-1 solutions; and (iii) to account for the relative mass difference, the ^{238/234}U and ^{238/236}U isotope ratios were normalised by multiplying them by 4/3 and 2/3 of the ^{238/235}U mass bias factor, respectively.