



**British
Geological Survey**

NATURAL ENVIRONMENT RESEARCH COUNCIL

Analysis of Soil Samples from Kosovo

DERA Project CU013-0918342

Waste and Pollution Management Programme
Commissioned Report CR/01/071N



BRITISH GEOLOGICAL SURVEY

COMMISSIONED REPORT CR/01/071N

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Key words

XRFS, lead, depleted uranium.

Front cover

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

Bibliographical reference

GOWING, C J B. 2001. Analysis
of Soil Samples from Kosovo.
*British Geological Survey
Commissioned Report,*
CR/01/071N. 10 pp.

Contents

Introduction	1
Sample receipt.....	1
Analytical scheme	2
Sample preparation	2
Geochemical analysis.....	4
Particle size analysis	6
Results	6
References.....	7
Appendix 1: Asbestos.....	8

Figures

Figure 1. Schematic flow diagram of the sample preparation route for soil samples.....	3
Figure 2. 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 and mean \pm 2 standard deviations (WL).....	6

Tables

Table 1. Sample weights, dose rates and potential of asbestos contamination.....	1
Table 2. Sub-samples and excess materials extracted during the sample preparation procedure.....	4
Table 3. Instrumental parameters of the Philips PW2400 Wavelength Dispersive X-Ray Fluorescence Spectrometer.....	5
Table 4. Pb and U concentrations in the 15 samples analysed.....	6

Introduction

A number of soil samples were collected from locations in Kosovo by staff of the Defense Evaluation and Research Agency (DERA). Twenty three samples were collected from DERA, Portsmouth and transported in two Aluminium trunks to 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.

During sampling at one site, VJ Barracks, it was noted that a building close to the sampling sites had had an asbestos roof. Consequently, 8 were identified as having suspicion of containing asbestos, in varying amounts from 'likely' to 'caution required' (Table 1).

Sample receipt

On receipt at BGS, the sealed aluminium trunks were placed into 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 61/01 3 was in a plastic tub.

Table 1. Sample weights, dose rates and potential of asbestos contamination.

Sample name	Sample weight (g)	Measured dose rate (μ 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	-
1 not adj	300	<0.1	caution required
3A	1100	0.5*	likely to contain asbestos
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
61/01 3	60	2.2*	caution required

* These samples will have had radiological dose re-monitored before preparation work is undertaken.

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, 3ADJ and 61/01 3) identified by the gamma ray spectrometry.

Analytical scheme

The 15 samples that were not potentially contaminated with asbestos have been prepared according to a sample preparation route, which ensured that the sample taken for analysis was representative of the original material. The final stage of the sample preparation was to press a pellet, which could then be analysed by X-Ray Fluorescence Spectrometry (XRFS). The feasibility of analysing the 8 potentially contaminated samples is currently under investigation.

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. At each stage any excess material was carefully bagged and labelled. Sub-samples and excess portions extracted during the sample preparation procedure are catalogued Table 2. The sample 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 could be compared on an even footing.

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 in nylon at 2 mm 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 $99\% \leq 50 \mu\text{m}$.

An aliquot of 12 g of the milled material was then mixed thoroughly with 3 g of a wax binder (a mixture of 9 parts EMU120FD styrene co-polymer (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. Excess material from the milling stage was retained for further work either for an additional XRFS pellet or for analysis by another method, e.g. inductively coupled plasma-mass spectrometry (ICP-MS).

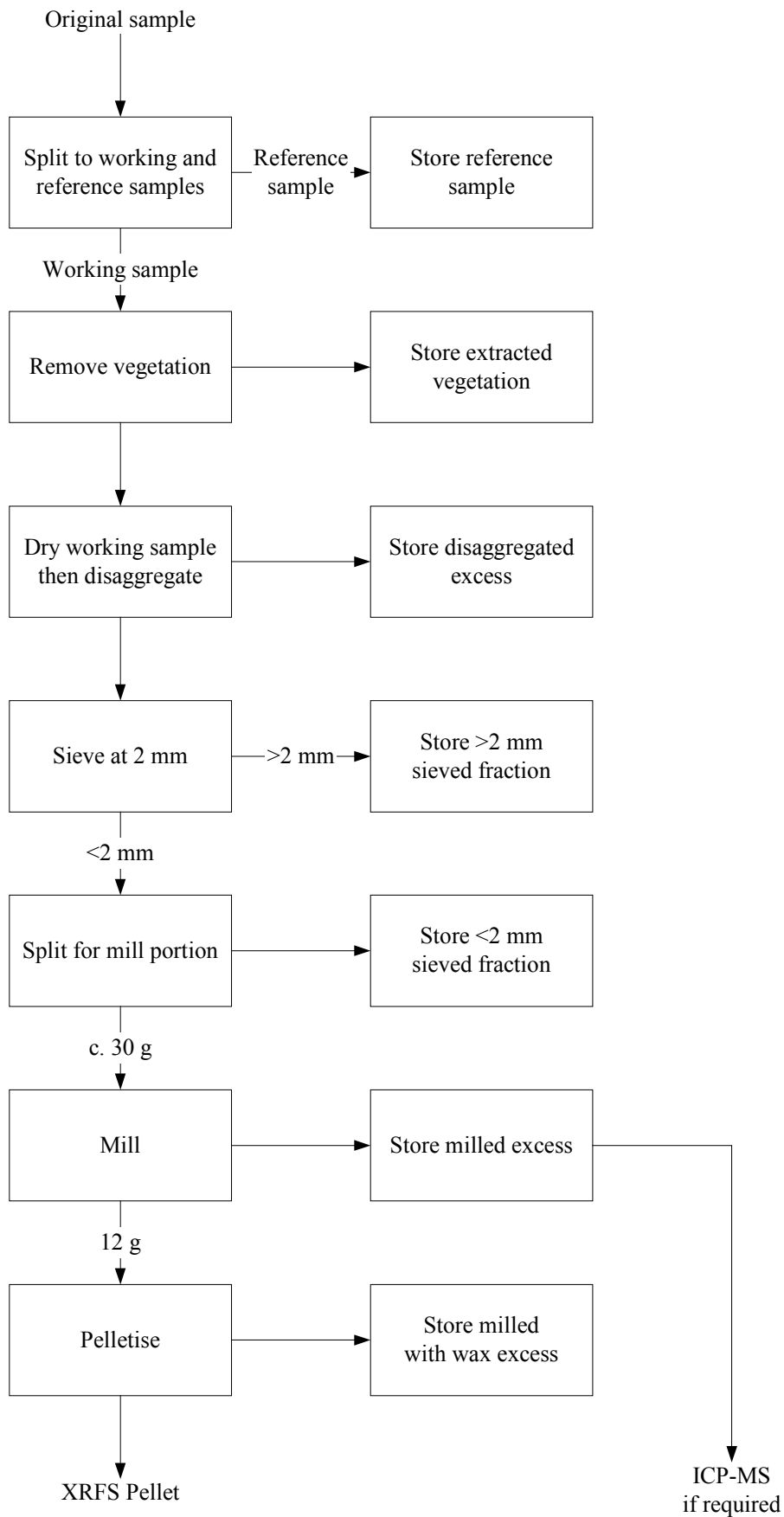


Figure 1. Schematic flow diagram of the sample preparation route for soil samples.

Table 2. Sub-samples and excess materials extracted during the sample preparation procedure.

Sample name	Reference sample	Vegetation	Disagg. excess	>2mm portion	<2mm excess	Milled excess	Mill with wax 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

No excess was produced after milling with wax binder.

Geochemical analysis

The BGS Analytical Geochemistry Laboratories were formally awarded accreditation by the United Kingdom Accreditation Service (UKAS) on 16 August 1999 and is 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. All activities in the Laboratories are subject to regular internal audits.

Major and trace element determinations for stream-sediment and soil samples are routinely carried out for a number of projects including the Geochemical Baseline Survey of the Environment (British Geological Survey, 1997 and in press) at BGS by both energy dispersive (ED) and wavelength dispersive (WD) XRFS (Ingham and Vrebos, 1994).

These pellets were analysed by WD-XRFS using a Philips PW2400 spectrometer, which is fitted with a 102 position sample changer and 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 3.

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 using the routine BGS method for determination of heavy metals.

In 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.

Table 3. 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		

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.

Routine laboratory Quality Control (QC) is monitored by daily analysis of 2 QC samples. Data from these analyses are 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 are re-analysed. One of the Shewhart charts, shown in Figure 2, 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.

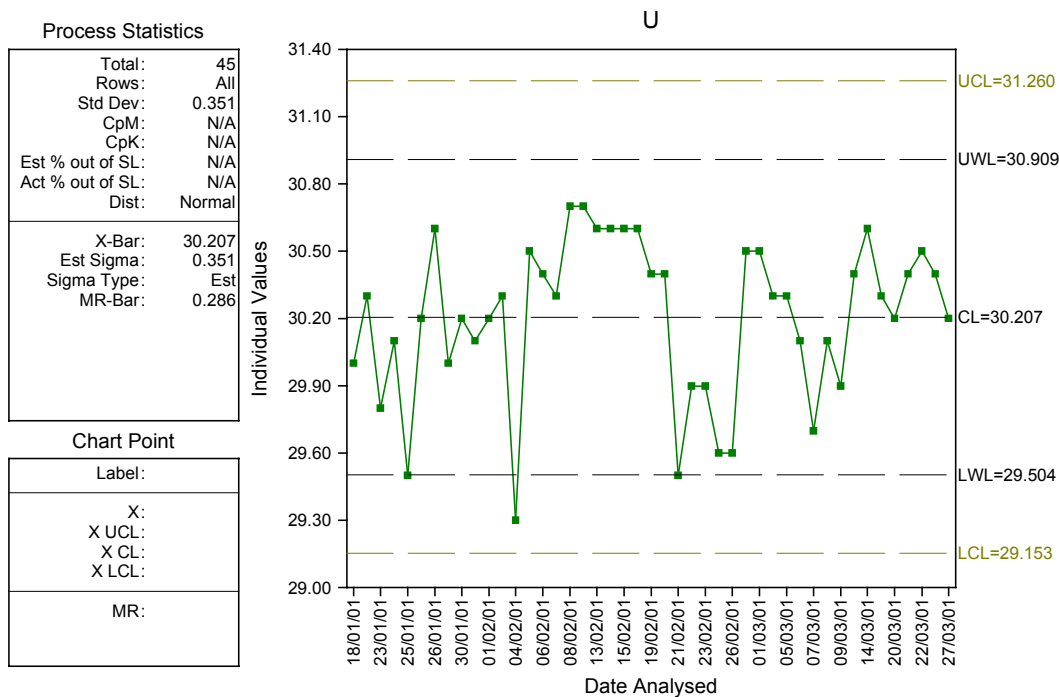


Figure 2. Shewhart chart of a QC sample for uranium analysed over a 10 week period. Upper (U) and Lower (L) Control Limits (CL) and Warning Limits (WL) are shown at mean \pm 3 standard deviations and mean \pm 2 standard deviations (WL).

Particle size analysis

None of the 15 samples analysed have had sufficient uranium concentration to warrant investigation by particle size analysis.

Results

The fully validated results for Pb and U concentrations are shown in Table 4.

Table 4. Pb and U concentrations in the 15 samples analysed.

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

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Appendix 1: Asbestos

Asbestos risk

The presence of asbestos presents a greater hazard than if only DU was present. The samples need to be processed without generating dust that exceeds acceptable hazard levels. It will not be possible to prepare the samples using the desired route as too great a risk would arise at nearly every stage and the surrounding laboratory and the routine air handling (local exhaust ventilation) units would themselves potentially become contaminated with asbestos-containing dust.

Most health and safety literature discusses the use of asbestos in much larger quantities than we are concerned with here. Nevertheless the low asbestos control limit¹ necessitates almost dust-free working environments, particularly considering the inhalable asbestos dust (<1 to 20 µm) is not visible to the naked eye.

External laboratories that do handle such materials typically do so for the purpose of identification of the form of asbestos present. Of those contacted, one will handle the samples only for this purpose and a second will, on finding asbestos, only analyse the sample as received, with no further drying or milling, by *aqua regia* leach followed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) or ICP-MS analysis.

An alternative analytical protocol

The preferred analytical scheme, validated and quantitative XRFS, requires that the sample is prepared in the specified manner and pressed into a pellet. Although is not feasible to follow this preparation route, an alternative route may be possible by analysing the samples as received, with no further preparation.

Such methods may include taking an aliquot of damp material (in order minimize dust generation), transferring to analytical vessel and carrying out either a total acid attack (HF/HNO₃/HClO₄/HCl) or a partial acid attack (*aqua regia* or HNO₃) then analysing the resultant solution by ICP-MS or ICP-AES. The total attack should dissolve asbestos, thereby removing the physical hazard and the partial attack (leach) would leave a wet residue that could be retained onto disposable tissue for return with excess material.

This approach would allow an estimation of the U content of the material, but could not be regarded as accurate or as precise as the XRFS method proposed, as discussed below:

1. Under ideal conditions, a sample is dried before analysis to remove the unknown and variable amount of water adsorbed onto particles and contained within the sample material. As drying can not take place, the different amount of water, both within any one sample and between similar samples, will introduce an unknown error.

¹ 0.5 fibre per ml of air, averaged over 4 hours, with a maximum of 1.5 fibres per ml of air, averaged over a continuous period of 10 minutes (Asbestos control: a safety rep's guide to prevention of exposure to asbestos Supplement, produced by the GMB Union).

2. Under ideal conditions, a dry sample is sieved to remove larger fragments of vegetation and other organic matter as well as larger granules and pebbles, the presence of which would dilute the apparent trace element levels.
3. It would be impractical to mill an entire sample, so, routinely, a large sample presented for analysis is repeatedly sub-divided following appropriate protocols, such as cone-and-quarter, to derive a sub-sample for the mill that is representative of the whole. Sub-sampling the whole sample by taking a sample for analysis at random will give rise to unknown errors, as the sample is unlikely to be sufficiently homogenous in this state.
4. Under ideal conditions, a split of a dry sample of a known size fraction is milled to disaggregate fully the soil and to break open most mineral grains greater than a specified target size, which in turn facilitates the chemical dissolution of the material. Attempting dissolution of a sample containing particles of widely different sizes would require the sample to be left in contact with the acid for different lengths of time, possibly also at different temperatures. The difference in these conditions would give rise to further errors.
5. Each of these stages helps to ensure that the sub-sample analysed is representative of the whole; water is driven off so that all samples can be compared on the same (dry) basis, coarse particles are removed so that all samples can be compared by analysis of the same specified size fraction, methodical sub-sampling ensures homogeneity and the sample is milled to ensure that the analytical aliquot is taken from a thoroughly mixed and homogenous powder. As none of these stages are feasible, the sample analysed is likely to be inhomogeneous.

An estimation of the errors that would be introduced because the normally employed preparation steps cannot be used can be made by analysis of a number of replicate sub-samples; 3 or 4 should be sufficient, to give an average concentration of the trace elements required.

Total acid attack or partial acid leach

The optimal digestion method would seem to be the total acid attack. However, this approach is not recommended due to the considerations made in point 4 above and such a small sample would introduce an unacceptable level of inhomogeneity, particularly when considering the potential inhomogeneous distribution of a wide range of particle sizes of DU.

A partial leach would liberate soluble metals and minerals from the soil and leave much of the silicate matrix unattacked. This method is not routinely used in BGS and has not been validated as the total acid attack method has. It would be necessary to assess the recovery of such a leach of U from natural minerals and from DU. Uranium metal is soluble in HNO₃, and so finely disseminated metallic particles of DU should go into solution easily; possibly this would be a good method for the determination of DU contaminated samples.

The suitability of a partial attack could be assessed from analysing some of the 15 samples already analysed by XRFS and some samples of DU (this will require looking into the hazards associated with the handling of open radioactive sources). Once the extent of the leach has been assessed then the 8 remaining samples could be in triplicate to give an estimation of the U concentration (and maybe the relative proportions of DU and natural uranium).

This work would be quite involved and BGS would not be able to start such work till the end of April 2001 due to present commitments. This approach is also outside the original quotation and would need to be charged as extra. An alternative approach would be to sub-contract the work to an external laboratory, but we would have no control over the validation status of such work.

Options available

1. If a risk assessment permits handling of samples as received, perform acid leach and ICP-MS analysis of the samples at BGS. Validation could be assessed, analysis would require extra cost and work is subject to a time delay.
2. Perform acid leach and ICP-AES/ICP-MS analysis of the samples at external laboratory. Validation status, timescale and extra cost are unknown.
3. Leave the samples unanalysed as the (potential) asbestos contamination presents too great a hazard.

The additional costs and time involved in following options 1 or 2 may render such work impractical and uneconomic. The hazard faced by presence of asbestos arguably outweighs the hazard associated with the presence of DU in these samples. It may be possible to proceed with further work if it is possible to specify which, if any, of the samples are actually contaminated with asbestos and to estimate the potential concentration.

If it is not possible to assess the asbestos content of these samples and DERA need some information on the hazard due to DU alone, then it will be necessary to perform analysis of similar sample types taken from an area where there is known to be no asbestos contamination.