Choosing a Multi-Element Technique for MCERTS Compliant Soil Analysis

ENVIRONMENTAL ANALYSIS

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Why monitor elements in soil?

Throughout the UK there are thousands of sites (estimated 300,000 hectares of land) which have been contaminated with environmentally harmful or potentially toxic materials from previous industrial land uses. The Government has targeted these "brown-field" sites as areas for reclamation and redevelopment in preference to new development on "green-field" sites. In order to preserve the countryside the Government has demanded that 60% of all new houses be built on brown-field sites.

With the passing of the Environment Act in 1995, the Environment Agency was formed, providing a new framework for regulation and its application. Within this new regime, the old Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) soil guideline values, which outlined acceptable concentrations of contaminants for various land uses, were replaced with the Contaminated Land Exposure Assessment (CLEA) model. The soil guideline values (SGVs) are shown in Table 1. Testing of soils for compliance with these values and in compliance with regulations such as Part IIA of the Environmental Protection Act 1990, Pollution, Prevention and Control (England and Wales Regulations) 2000 and Waste Management Licensing Regulations 1994, is performed by many laboratories.

What is MCERTS?

The Environment Agency's Monitoring Certification Scheme (MCERTS) is intended to deliver quality environmental measurements by providing for the product certification of instruments, the competency certification of personnel and the accreditation of laboratories. In 2004 the scheme was expanded to include chemical testing of soils by publication of a performance standard for all laboratories involved in the chemical testing of soils for regulatory purposes. The Agency's MCERTS website gives further information (see www.mcerts.net).

What are the options for analysis?

For laboratory analysis of soils, a sample is prepared by drying, and sieving and then a test portion is subjected to a digestion with strong acid. The extract is analysed with an appropriate atomic spectrometry technique, such as atomic absorption (AA), inductively coupled plasma emission spectrometry (ICP) or inductively coupled plasma mass spectrometry (ICP-MS). Normally information on multiple elements is required. Consequently AA, which is capable of analysing only a single element at a time, is deemed too inefficient for all but the very lowest of sample numbers. Most modern analytical labs limit their choice to ICP or ICP-MS, but which is most suitable?

ICP is more tolerant of the typically high levels of sample matrix present in such digests, but has poorer detection limits. ICP-MS, on the other hand, is capable of detecting extremely low concentrations, but is traditionally somewhat sensitive to 'physical interferences' caused by the presence of high concentrations of sample matrix components in the solution. This tends to manifest itself in a suppression of the analyte signal when compared to that observed in a 'clean' solution and also a drift of signal intensity with time. In order for ICP-MS to produce satisfactory data, digests of this type must be diluted to reduce the effects of these physical interferences, compromising the detection capability of the technique. ICP, being less sensitive to the effects of sample matrix, does not require such large dilutions, but exhibits poorer detection capability. This raises the question of which technique produces the best performance when the trade-off between dilution and sensitivity is taken into account?

Method
Sample preparation

Known reference samples (LGC Promochem, Teddington, UK) were used in order to check the accuracy of metal determinations (see Table 2). Samples were prepared by accurately weighing a 3g portion of each soil into a boiling tube. An aliquot of 22.5cm³ of concentrated hydrochloric acid (SPA Grade, Romil, Cambridge, UK), and an aliquot of 7.5cm³ of concentrated nitric acid (SPA Grade, Romil, Cambridge, UK) were added to the tube, forming aqua regia. The tube was fitted with a reflux condenser and placed into the rack of an automated digestion block (SMA, C. Gerhardt, Koenigswinter, Germany). The mixture was left at room temperature for 2 hours to allow slow oxidation of organic material to occur. The samples were digested by ramping linearly to a temperature of 180ºC over a period of one hour. This temperature was maintained and the mixture refluxed for 2 hours, after which a cooling period of 30 minutes, out of the heating block, was allowed. The condensers were washed into the boiling tubes with small portions of deionised water (18.2M Ohm cm resistivity, Millipore, Watford, UK) and the contents of the tube were quantitatively transferred to a 200 cm³ volumetric flask. The samples were made to a final volume of 200cm³ with deionised water. Blank digestions were performed in an identical manner, but omitting the sample, to check for contamination.

Table 1: Soil guideline values for elemental contaminants (mg/kg) from the ICRCL guidance and the CLEA model

| Element | ICRCL Figures | | | CLEA Figures | | |
	Residential with plant uptake	Parks and open spaces	Residential with plant uptake	Residential	Allotments	Commercial /Industrial
As	10	40	20	20	20	500
B	3	–	–	–	–	–
Cd	3	15	1 (pH 6) 2 (pH 7) 8 (pH 8)	30	1 (pH 6) 2 (pH 7) 8 (pH 8)	1400
Cr	600	1000	130	200	130	5000
Cu	130	–	–	–	–	–
Hg	1	20	8	15	8	480
Ni	70	–	50	75	50	5000
Pb	500	2000	450	450	450	750
Se	3	6	35	260	35	8000
Zn	300	–	–	–	–	–

Table 2: Descriptions and reference values, in mg/kg, of the soil CRMs used

Description	LGC 6144 Gas works contaminated soil	RTC-CRM046 Clay soil	RTC-CRM038 Loam soil
As	14.9	7.47	25
B	–	–	120
Ba	–	–	324
Be	–	–	257
Cd	–	7.01	87
Co	–	8.22	84.7
Cr	118	45.7	129
Cu	71	62.2	115
Fe	–	–	12800
Hg	0.53	0.153	44.4
Mn	–	118	506
Mo	–	–	311
Ni	27	37.5	131
Pb	196	45.3	128
Sb	–	–	141
Se	0.71	–	176
Sn	–	–	156
Tl	–	–	166
V	38	–	88.8
Zn	192	114	476

The resultant solutions contain a maximum of 15% aqua regia and 1.5% total dissolved solids. This is satisfactory for direct analysis by ICP, but is somewhat too concentrated for ICP-MS, for which a further 5-fold dilution was performed with deionised water. This results in a maximum solution composition of 3% aqua regia and 0.3% total dissolved solids.

When mercury analysis is required, some additional precautions are needed. Mercury tends to exhibit stability problems in solutions and is frequently lost, probably through reduction of Hg^{2+} to the groundstate, which is then lost as a vapour. Mercury is however quite stable in the strongly oxidising aqua regia digestate solution. When the solutions are further diluted for ICP-MS analysis, it may be necessary to take further precautions to stabilise mercury by adding gold (from 1000 mg/L stock, SPEX, Middlesex, UK) at approximately 0.5 mg/L to each solution. It is thought that gold stabilises the mercury due to its higher redox potential.

Analysis details

Calibration

Calibration solutions were prepared for ICP and ICP-MS based on expected solution concentrations for typical soil samples prepared in this manner. Table 3 shows the calibration concentrations and matrices used.

Table 3: Calibration and QC standard concentrations, in mg/L (except where indicated), for ICP and ICP-MS

Analyte	Std1	Std2	Std3	QC Std	Spike Level (mg/kg)	Std1	Std2	Std3	QC Std	Spike Level (mg/kg)
	Standards for ICP Analysis					**Standards for ICP-MS Analysis**				
As	0.05	0.1	0.5	0.25	23	0.01	0.02	0.1	0.05	70
B	0.05	0.1	0.5	0.25	23	0.01	0.02	0.1	0.05	70
Ba	0.5	1	5	2.5	233	0.1	0.2	1	0.5	700
Be	0.05	0.1	0.5	0.25	23	0.01	0.02	0.1	0.05	70
Cd	0.05	0.1	0.5	0.25	23	0.01	0.02	0.1	0.05	70
Co	0.05	0.1	0.5	0.25	23	0.01	0.02	0.1	0.05	70
Cr	0.5	1	5	2.5	233	0.1	0.2	1	0.5	700
Cu	2.5	5	25	12.5	1167	0.5	1	5	2.5	3500
Fe	25	50	250	125	11668	5	10	50	25	35000
Hg	0.0025	0.005	0.025	0.0125	1	0.0005	0.001	0.005	0.0025	3.5
Mn	2.5	5	25	12.5	1167	0.5	1	5	2.5	3500
Mo	0.1	0.2	1	0.5	47	0.02	0.04	0.2	0.1	140
Ni	0.5	1	5	2.5	233	0.1	0.2	1	0.5	700
Pb	0.5	1	5	2.5	233	0.1	0.2	1	0.5	700
Sb	0.05	0.1	0.5	0.25	23	0.01	0.02	0.1	0.05	70
Se	0.05	0.1	0.5	0.25	23	0.01	0.02	0.1	0.05	70
Sn	0.05	0.1	0.5	0.25	23	0.01	0.02	0.1	0.05	70
Tl	0.05	0.1	0.5	0.25	23	0.01	0.02	0.1	0.05	70
V	0.5	1	5	2.5	233	0.1	0.2	1	0.5	700
Zn	2.5	5	25	12.5	1167	0.5	1	5	2.5	3500
Matrices	**15% Aqua Regia**					**3% Aqua Regia, 0.5 mg/L Au**				

Wash Solution

Wash solutions of the same composition as the sample diluent were used to rinse the sample introduction equipment between each sample, i.e. 15% aqua regia for ICP and 3% aqua regia (including 0.5 mg/L gold for mercury washout) for ICP-MS.

Internal Standardisation

No internal standards were used for ICP measurements. Since ICP-MS is somewhat more susceptible to suppression, it is standard practice to use internal standards, which were added on-line. The internal standard solution contained 0.5 mg/L isotopically enriched lithium-6, 0.2 mg/L germanium, and 0.01 mg/L rhodium and lutetium in the same matrix as the other solutions for ICP-MS analysis.

Quality Control

Quality control (QC) solutions were independently prepared at 20% of the calibration range and run at a frequency of once every 10 samples (see Table 3). Additionally, samples were spiked to check for matrix effects through spike recovery calculation. The spike concentrations in mg/kg equivalent are shown in Table 3. The spike for ICP is somewhat lower due to the difficulty of spiking high concentrations into a relatively low volume of solution. This affected the spike recoveries for ICP for samples containing higher concentrations of analytes. The concentrations present in the CRM RTC-CRM038 are somewhat higher than those found in the other two CRMs and the spike levels were considered inappropriate for this sample and are therefore not shown.

Analytical Procedure

The procedure used here is not intended to be a full MCERTS performance assessment, but rather an indication of the performance levels achievable. Each sample was digested in duplicate and each resulting solution was analysed a total of six times with ICP and ICP-MS. Each of these six analyses was performed against a new calibration. The QC sample was run at a frequency of once every 10 samples to check for calibration accuracy and instrument drift. Results within 10% of the known QC value were deemed acceptable. Blank samples were run in duplicate in each analysis batch in a randomised order and were used to calculate the method detection limit (MDL).

Instrument Details

An iCAP 6500 Duo ICP (Thermo Electron Corp., Cambridge, UK) and an XSeries^{II} ICP-MS with collision cell technology (Thermo Electron Corp., Bremen, Germany) were used to analyse the samples. Table 4 gives the lines and views used for the ICP measurements and the masses and modes used for ICP-MS analysis.

Table 4: View, wavelengths, modes and masses for ICP and ICP-MS measurements, respectively

Analyte	View	Wavelength (nm)	Mode	Mass (amu)
	Conditions for ICP Analysis		**Conditions for ICP-MS Analysis**	
As	Axial	189.0	He CCT	75
B	Axial	208.9	Standard	11
Ba	Radial	455.4	Standard	137
Be	Axial	313.1	Standard	9
Cd	Axial	214.4	Standard	111
Co	Axial	228.6	He CCT	59
Cr	Axial	267.7	He CCT	52
Cu	Radial	324.7	He CCT	63
Fe	Radial	271.4	He CCT	56
Hg	Axial	184.9	Standard	202
Mn	Radial	257.6	He CCT	55
Mo	Axial	202.0	Standard	98
Ni	Axial	231.6	He CCT	60
Pb	Axial	220.3	Standard	208
Sb	Axial	206.8	Standard	121
Se	Axial	196.0	H2 CCT	78
Sn	Axial	189.9	Standard	118
Tl	Axial	190.8	Standard	205
V	Axial	292.4	He CCT	51
Zn	Radial	206.2	He CCT	66

Results

Table 5 gives the corrected method detection limits (MDLs) for ICP and ICP-MS as calculated from the 5-sigma model from the results of paired blank analyses and compares them with the lowest SGVs from the CLEA model (or ICRCL guidelines). Table 6 gives the results of the multiple analyses of the QC standards analysed. Tables 7 to 12 show the mean results of the analysis of the CRM samples, the relative standard deviations (RSDs) and the spike results and recoveries. For the sake of brevity, all sample data has been pooled.

Table 5: MDLs for ICP and ICP-MS in mg/kg

Analyte	Lowest SGV	ICP	ICP-MS
As	20	0.3	0.2
B	(3)	60	0.4
Ba	–	3	0.05
Be	–	0.05	0.1
Cd	1	0.02	0.05
Co	–	0.07	0.1
Cr	130	2	0.1
Cu	(130)	0.8	1
Fe	–	100	1
Hg	8	0.3	0.03
Mn	–	2	0.1
Mo	–	0.2	0.1
Ni	50	1	0.05
Pb	450	1	0.05
Sb	–	0.2	0.02
Se	35	0.4	0.3
Sn	–	1	0.03
Tl	–	0.2	0.1
V	–	0.2	0.1
Zn	(300)	2	1

Table 6: Results of analyses of QC standards (mg/L)

Analyte	ICP QC Results			ICP-MS QC Results		
	Mean	RSD %	Recovery %	Mean	RSD %	Recovery %
As	0.25	0.9	101	0.049	4.0	98
B	0.25	1.5	99	0.052	4.5	105
Ba	2.54	1.2	102	0.496	4.7	99
Be	0.25	3.0	100	0.051	3.7	103
Cd	0.26	1.9	102	0.051	3.4	102
Co	0.26	3.9	105	0.051	3.2	102
Cr	2.50	0.4	100	0.503	3.6	101
Cu	12.8	2.3	102	2.64	3.5	106
Fe	128	3.0	102	25.06	3.4	100
Hg	0.01	7.0	109	0.0027	4.5	107
Mn	12.6	0.7	100	2.457	3.3	98
Mo	0.52	4.0	104	0.100	4.0	100
Ni	2.56	1.5	102	0.509	3.2	102
Pb	2.53	1.4	101	0.504	4.3	101
Sb	0.26	4.1	104	0.050	4.6	100
Se	0.26	3.9	104	0.052	3.6	105
Sn	0.26	2.7	104	0.050	4.1	100
Tl	0.26	1.8	103	0.051	4.8	101
V	2.45	1.8	98	0.502	3.6	100
Zn	12.5	1.7	100	2.488	3.4	100

Table 7: ICP results for LGC 6144 (mg/kg)

Analyte	LGC 6144				Spike	
	Measured	RSD %	Recovery %	Measured	RSD %	Spike Recovery %
As	14.3	3.0	96	35.6	4.1	96
B	<DL	1.2	-	31.1	1.6	90
Ba	129	1.3	-	358	1.8	102
Be	0.6	1.8	-	23.0	3.4	96
Cd	0.6	21.7	-	20.5	9.6	86
Co	7.4	1.6	-	28.2	6.1	91
Cr	104	0.2	88	305	1.9	89
Cu	58.9	1.9	83	1240	1.7	102
Fe	32300	0.9	-	42000	2.6	102
Hg	0.4	5.7	77	1.6	8.5	101
Mn	520	0.5	-	1600	3.1	96
Mo	6.9	2.2	-	50.6	5.0	95
Ni	26.5	3.2	98	236	1.7	90
Pb	164	1.8	84	344	3.1	82
Sb	5.3	3.1	-	26.4	9.7	92
Se	0.8	2.6	106	24.5	2.3	102
Sn	14.5	1.2	-	35.1	1.3	93
Tl	<DL	-	-	19.8	6.3	89
V	30.5	0.7	80	245	1.5	93
Zn	166	1.4	85	1250	3.4	94

Table 8: ICP-MS results for LGC 6144 (mg/kg)

Analyte	LGC 6144				Spike	
	Measured	RSD %	Recovery %	Measured	RSD %	Spike Recovery %
As	16.7	4.3	112	81.5	1.8	93
B	13.2	4.0	-	80.4	3.4	96
Ba	136	1.9	-	821	4.7	98
Be	0.66	14.7	-	68.7	3.5	97
Cd	0.34	31.5	-	69.0	4.0	98
Co	8.27	4.5	-	72.8	1.7	92
Cr	120	4.0	101	767	2.1	93
Cu	69.3	4.0	98	3309	2.6	93
Fe	35300	2.7	-	67300	1.2	92
Hg	0.55	9.7	105	3.83	4.3	94
Mn	622	3.7	-	3880	1.9	93
Mo	7.47	1.6	-	145	2.9	98
Ni	32.0	3.0	119	674	2.1	92
Pb	200	3.1	102	856	3.5	94
Sb	4.42	2.4	-	69.0	4.7	92
Se	0.43	126.9	61	70.1	9.5	99
Sn	17.4	2.2	-	86.2	4.1	98
Tl	0.11	75.0	-	67.1	3.1	96
V	36.3	3.7	95	687	1.8	93
Zn	197	3.3	103	3410	1.5	92

Table 9: ICP results for RTC-CRM042 (mg/kg)

Analyte	RTC-CRM042				Spike	
	Measured	RSD %	Recovery %	Measured	RSD %	Spike Recovery %
As	7.4	7.5	99	29.6	0.7	97
B	<DL	1.2	-	29.1	1.4	92
Ba	123	1.4	-	368	5.5	109
Be	0.9	3.1	-	25.1	5.7	104
Cd	6.5	5.4	93	26.0	14.8	85
Co	7.0	1.9	86	28.5	7.8	94
Cr	46.1	0.3	101	258	3.8	92
Cu	51.4	2.1	83	1240	2.2	103
Fe	21500	1.5	-	32600	2.9	108
Hg	0.1	21.8	87	1.3	10.4	102
Mn	101	1.2	86	1280	6.5	102
Mo	0.6	3.2	-	46.5	6.1	98
Ni	30.8	3.1	98	251	1.4	95
Pb	35.0	0.5	77	235	6.4	87
Sb	2.0	7.4	-	23.3	14.5	92
Se	0.7	50.4	-	24.9	0.6	104
Sn	7.5	1.2	-	29.9	0.8	98
Tl	<DL	-	-	20.7	6.6	93
V	50.7	0.6	-	268	1.5	95
Zn	96.6	1.9	85	1250	4.3	100

Table 10: ICP-MS results for RTC-CRM042 (mg/kg)

Analyte	RTC-CRM042				Spike	
	Measured	RSD %	Recovery %	Measured	RSD %	Spike Recovery %
As	7.48	4.9	100	75.3	2.6	97
B	9.25	4.2	-	79.6	4.8	100
Ba	126	3.0	-	809	5.9	98
Be	0.88	14	-	69.7	4.6	98
Cd	6.98	3.0	100	75.1	5.0	97
Co	7.13	3.5	87	72.9	1.9	94
Cr	50.0	3.5	109	713	2.5	95
Cu	57.8	4.7	93	3340	3.1	94
Fe	22300	2.2	-	56200	3.2	97
Hg	0.11	12	69	3.41	5.4	94
Mn	118	3.1	100	3450	2.4	95
Mo	0.49	19	-	138	5.4	98
Ni	34.7	3.5	92	690	2.6	94
Pb	43.3	3.5	95	695	5.1	93
Sb	1.45	3.1	-	68.8	5.7	96
Se	0.09	659	-	72.4	5.6	103
Sn	8.62	3.0	-	76.4	5.2	97
Tl	0.17	90	-	66.8	5.0	95
V	57.2	3.9	-	726	2.9	96
Zn	105	3.3	92	3350	2.6	93

Tables 11: ICP results for RTC-CRM038 (mg/kg)

Analyte	RTC-CRM038		
	Measured	RSD %	Recovery %
As	25.1	8.5	101
B	120	0.7	100
Ba	316	3.1	98
Be	217	2.5	85
Cd	77.8	1.2	89
Co	74.2	2.5	88
Cr	116	0.3	90
Cu	98.3	3.5	85
Fe	13400	1.1	105
Hg	41.4	1.8	93
Mn	434	2.1	86
Mo	299	2.9	96
Ni	108	2.3	83
Pb	105	1.2	82
Sb	232	2.4	164
Se	161	2.1	91
Sn	141	2.3	90
Tl	151	6.1	91
V	81.2	0.8	91
Zn	413	2.0	87

Tables 12: ICP-MS results for RTC-CRM038 (mg/kg)

Analyte	RTC-CRM038		
	Measured	RSD %	Recovery %
As	25.1	2.6	100
B	136	2.5	113
Ba	337	1.9	104
Be	266	3.0	103
Cd	90.7	3.2	104
Co	81.6	1.2	96
Cr	128	1.7	100
Cu	114	2.4	100
Fe	14050	1.9	110
Hg	43.6	4.3	98
Mn	514	1.4	102
Mo	331	3.0	106
Ni	126	1.6	96
Pb	124	3.2	97
Sb	141	2.6	100
Se	199	4.4	113
Sn	162	3.1	104
Tl	163	3.5	98
V	96.0	1.7	108
Zn	468	0.9	98

Discussion

MDLs

The method detection limits (MDLs) for ICP-MS are generally 1-3 orders of magnitude lower than those of ICP in terms of in-solution values, however, when the extra dilution applied to the solutions for ICP-MS analysis is considered and the MDLs are converted to mg/kg in the solid sample, there is little difference between the techniques. Notable exceptions include boron and iron which were markedly improved with ICP-MS, although the most sensitive ICP lines were not used. Low detection limits are, however, not required for iron which is normally present at high concentrations in soils. Elements that require low detection limits include arsenic, selenium, mercury and cadmium. With the exception of mercury, which is significantly lower with ICP-MS, all detection limits for these elements are similar and satisfactorily low with either technique. There are no specific requirements for MDLs within the MCERTS performance specification, but comparing the MDLs with the lowest soil guideline values (see Table 5), either technique normally produces values that are at least 1 order of magnitude lower than the SGV. Therefore either technique is capable of providing the detection power required.

Accuracy

Accuracy is assessed in three ways:

1. by assessing QC results;
2. by assessing CRM results; and
3. by assessing spike recovery results.

The first checks the instrumental measurement accuracy, the second checks the extraction and instrumental determination and the third checks for matrix effects in the sample. MCERTS requires that the overall accuracy for most metallic species is within 10% of the certified concentration in a CRM or the expected value in a spike, with the exception of arsenic and antimony which must be within 15%. The instrumental determinations are easily capable of this level of accuracy, as shown by the QC results in Table 6. When the extraction process is taken into account, the vast majority of analytes measured in CRMs by both techniques are within 20%. Some analytes exhibit accuracy outside the MCERTS requirements, most producing low recoveries. This is most likely due to problems with completeness of extraction of these elements from the solid samples. ICP tends to exhibit lower recoveries than ICP-MS, possibly due to some uncorrected suppression effects since the ICP-MS measurements were corrected with internal standards, while ICP measurements were not. The spike recoveries give information about matrix effects and are generally closer to the expected results than are the CRM recoveries. This shows that matrix effects are not particularly prevalent and that most of the problems with low recoveries for the CRMs are due to incomplete extraction. Some of the high recoveries may be due to spectral interferences.

Precision
Measurement precision is assessed by comparing the magnitude of the relative standard deviation of results for each sample with the requirements specified in MCERTS. These are 5% for all elements, except antimony and arsenic, which are 7.5%. The RSDs for both techniques are generally less than 5% and are similar between the two techniques (see Table 6). Some exceptions are observed for the CRMs. When the variability of digestion is also considered, the precision is inferior. As expected, precision is noticeably poorer when the concentrations are close to the detection limit.

Conclusion

**Both techniques will do the job: ICP is simpler,
but ICP-MS gives better detection power where it's needed.**

Both techniques are suitable for the task of analysing soils digests, although ICP-MS produces slightly better detection limits – even after the extra dilution is taken into account – for some low concentration elements, especially mercury. This comes at the cost of an extra sample preparation step in the form of further dilution, the need to add gold for the stabilisation of mercury and the necessity to add internal standards, although this can be done very conveniently using a mixing tee. The benefit of ICP, on the other hand, is its simplicity and robustness to exposure to high matrix samples without dilution.

Elements: If they're not part of the solution, they're part of the problem!

Both techniques can easily produce adequate accuracy and precision when the target value is significantly above the detection limit as shown in Table 5. The greatest challenge in hitting the MCERTS accuracy and precision requirements, however, are at the sample preparation end of the process. The extraction efficiency of an element is dependent upon many factors including the chemical nature of the element, the sample matrix, the extraction medium and concentration, and the heat, pressure and length of contact during extraction. Essentially, if the element has not been extracted successfully, the result will be inaccurate and furthermore, if the extraction conditions are not consistent, the precision will be poor. The aqua regia extractions used during this work are based on the ISO 11466:1995 method and variants of this are widely used. This essentially fixes the extraction medium and the only variables are therefore the temperature and contact time. With hotplate digestions, hot spots and cold spots would commonly be seen and the vigorousness of the

reflux would frequently vary with the position of the vessel on the hotplate. Hotblock digesters, such as the one used here, help to reduce this variability and improve the precision, but do not necessarily ensure that the 'total' fraction of the metal is extracted. The problem is that aqua regia does not attack the silicate fraction of the soil and therefore metals bound within this fraction will not be extracted into the solution. Furthermore, refractory elements that form passive oxides, such as chromium and molybdenum, are unlikely to undergo complete extraction in an oxidising medium such as aqua regia. CRM manufacturers have attempted to overcome these latter problems by certifying CRMs with 'aqua regia extractable' values. However, these quite often have large uncertainties associated with their certified values due to the variability of extraction efficiency. It appears that the inherent variability of this part of the analytical process has not been taken fully into account by the Environment Agency when the performance standard for MCERTS was proposed. Consequently, many laboratories experience difficulties when attempting to meet the MCERTS performance requirements. It is proposed that a re-evaluation of the accuracy and precision targets for MCERTS to take this natural variability into account would be of benefit.

In final conclusion, plasma-based atomic spectrometry techniques provide an accurate, precise and powerful analytical approach for this important environmental monitoring task and modern instruments can easily meet the analytical performance requirements for the measurement part of the determination. Recent developments in interface and interference removal technology also allow some modern ICP-MS instruments to be used with less dilution and for a larger number of elements than in the past, making the technique much more suitable for the analysis of complex matrix samples. At the same time, some modern dual view ICPs give greater detection power than ever, allowing them to compete with ICP-MS in the detection limit war.

So, which is the technique of choice? Ultimately it comes down to the aspects of greatest importance to the individual lab:
• if the very lowest detection limits are key, ICP-MS is the best bet;
• if simplicity and robustness are more important, choose ICP.