

Direct Analysis of Undiluted Soil Digests Using the Agilent High Matrix Introduction Accessory with the 7500cx ICP-MS

Agilent has developed the High Matrix Introduction (HMI) accessory for ICP-MS as an alternative to conventional dilution. The HMI modifies the sample introduction system of the Agilent 7500 Octopole Reaction System (ORS) ICP-MS, making it possible to directly measure sample solutions with total dissolved solids (TDS) exceeding 1%. In collaboration with the Eurofins Analytico laboratory in the Netherlands, a 7500cx/HMI was used to directly measure high TDS soil extracts in compliance with Dutch regulatory guidelines. The results show that the HMI is a suitable replacement for conventional autodilution, allowing Analytico to use a single 7500cx/HMI ICP-MS in place of several instruments, including conventional ICP-MS, ICP-OES and a dedicated mercury analyzer.

Compared to ICP-Optical Emission Spectroscopy (ICP-OES) or other non-MS-based techniques, this has been considered an inherent limitation of ICP-MS. To compensate for this limitation, samples with total dissolved solids (TDS) levels higher than 0.1 to 0.2%, depending on the matrix, typically require dilution before measurement by ICP-MS, relying on ICP-MS's high sensitivity to compensate for the sensitivity loss due to dilution. However, conventional sample dilution has a number of other disadvantages, including reduced productivity, introduction of contaminants, dilution factor errors, and increased waste volume. As a superior alternative to conventional dilution, Agilent has developed a simple, novel modification to the sample introduction system of the Agilent 7500 ICP-MS with Octopole Reaction System (ORS) that can significantly improve the tolerance to high-matrix samples. The Agilent High Matrix Introduction (HMI)¹ accessory reduces sample matrix load on the plasma, making it possible to directly measure sample solutions with TDS exceeding 1%. As a result, samples previously measurable only by ICP-OES can now be measured directly by ICP-MS, using a 7500 ORS fitted with HMI. In this work, an Agilent 7500cx/HMI was used to test the system's ability to directly measure high TDS soil extracts in aqua regia and meet Dutch regulatory guidelines for reporting limits and data quality.

Direct Analysis of Aqua Regia Digests of Soils Using HMI-ICP-MS

This work was done in collaboration with the Eurofins Analytico laboratory (Analytico Milieu) in the Netherlands. Analytico has been part of the Eurofins group since 2001. Eurofins is a bio-analytical company with approximately 50 laboratories distributed over France, Germany, the UK, Denmark, Norway, Switzerland, and the United States. One of three divisions within Analytico, Analytico Milieu's expertise extends to the analysis of soil, sludge, groundwater, wastewater, air, building materials and residual matter, and, additionally, method development, validation, logistics, project management, and data management.

RF power (W)	1600
Carrier gas (L/min)	0.28
HMI dilution gas (L/min)	0.67
Aerosol dilution factor	1/12
Sample uptake rate (mL/min)	0.17
ISTD uptake rate (mL/min)	0.17
Total nebulizer flow (mL/min)	0.34
Extract 1 (V)	0
Extract 2 (V)	-160
He flow (He mode)	4.0 mL/min
KED (He mode)	2 volts
H ₂ flow (H ₂ mode)	4.0 mL/min
KED (H ₂ mode)	2 volts

Table 1. Instrument Tune Conditions (Values relating to HMI are shaded.)

Introduction

The determination of trace elements in high-matrix samples has always been a difficult analytical challenge. While inductively coupled plasma mass spectrometry (ICP-MS) has unsurpassed detection capability for trace metals, the potential for salt accumulation on the MS interface has always required that dissolved solids levels be limited. Furthermore, extremely corrosive or acidic samples can damage conventional ICP-MS interface components, including the sampler and skimmer cones, requiring the use of platinum or other expensive components.

In this collaboration, an Agilent 7500cx equipped with the HMI was used to generate performance data to be used for compliance with the Dutch regulation pertaining to contaminated soils (AS3000). Due to the high TDS levels and high acid concentrations of digested soils, dilution is necessary prior to analysis by ICP-MS. Analytico currently uses the Agilent Integrated Sample Introduction System (ISIS) to perform online dilutions to meet these requirements. However, the limitations of conventional dilutions prompted Analytico to evaluate the potential of HMI as a faster, simpler, less expensive replacement for conventional autodilution that would also eliminate the maintenance issues associated with a conventional autodilutor.

Analyte	Soil dry wt (mg/kg)	After 50x dilution (µg/L)
Cd	0.17	3.4
Cr	15	300
Cu	5	100
Ni	3	60
Pb	13	260
Zn	17	340
Hg	0.05	1
As	4	80
Ag	1	20
Se	10	200
Sb	1	20
Sn	6	120
Ba	15	300
Co	1	20
Mo	1.5	30
V	1	20
Be	0.1	2
Te	10	200
Tl	3	60

Table 2. Analytico 3-Sigma Required Detection Limits for Soils

Instrumentation

An Agilent 7500cx ICP-MS with the second peripump option for high sample throughput was equipped with the HMI. A Burgener MiraMist nebulizer was used. Instrument tune parameters, including HMI settings, are listed in Table 1. The plasma was optimized in ultra robust mode with 1/12 aerosol dilution. This is the maximum dilution factor that can be set with HMI and is approximately equivalent to diluting the sample x12 conventionally. All analytes except selenium were acquired in helium collision mode, thus eliminating the need for no-gas mode and the associated time required for mode switching. Selenium was acquired in hydrogen reaction mode due to the low detection limits required.

Sample Preparation

Actual soil samples received from Analytico's customers were prepared by adding 1 gram of soil to 8 mL of aqua regia prior to microwave digestion. Digested samples were then diluted to 50 mL final volume in ultra pure (18.2 MΩ) water. The final acid concentration is 4% HNO₃ and 12% HCl.

Calculation of Method Detection Limits (MDLs)

Since the HMI is effectively applying a dilution, the effects on detection limits are of critical importance. While ICP-MS possesses high sensitivity, the requirement for ultra trace detection limits in high TDS samples can still be challenging. Analytico has required MDLs for most analytes (based on a 1-g soil sample diluted to a final volume of 50 mL; see Table 2), which must be met in order for them to meet their reporting limits and satisfy Dutch regulatory requirements.

MDLs were calculated as 3-sigma of 10 replicates of a low-level (between one to three times the required MDL) spiked sand sample measured consecutively and also measured on 10 different days over a 30-day period² (Table 3). For all regulated elements, the calculated MDLs exceeded the Dutch regulatory requirements by nearly an order of magnitude or better. So with the HMI operating at maximum effective dilution, the system has ample sensitivity for the application.

Analyte - isotope	ORS mode	MDL (1) (mg/kg)	MDL (2) (mg/kg)	Dutch required MDL (mg/kg)
Be 9	He	0.042	0.046	0.1
V 51	He	0.255	0.481	1
Cr 52	He	2.300	4.517	15
Co 59	He	0.147	0.348	1
Ni 60	He	0.770	0.922	3
Cu 63	He	0.502	1.303	5
Zn 66	He	1.704	3.104	17
As 75	He	0.549	1.079	4
Se 78	H ₂	0.832	2.041	10
Se 78	He	1.064	1.991	10
Mo 95	He	0.195	0.413	1.5
Ag 107	He	0.278	0.701	1
Cd 114	He	0.058	0.066	0.17
Sn 118	He	0.589	1.353	6
Sb 121	He	0.333	0.401	1
Te 125	He	1.217	2.112	10
Ba 135	He	3.041	6.227	15
Hg 201	He	0.014	0.025	0.05
Tl 203	He	0.285	0.546	3
Pb 208	He	1.197	2.844	13

Table 3. Calculated Method Detection Limits (mg/kg) According to the Requirements of Dutch Regulation AS3000
MDL(1) = 3 σ of 10 replicates taken on the same day
MDL(2) = 3 σ of 10 replicates taken on different days¹

Analyte	ORS Mode	FeNeLab River Clay			BCR-144R Sewage Sludge		
		Measured mg/kg (ave, n = 10)	Certified mg/kg	Rec. % (ave)	Measured mg/kg (ave, n = 10)	Certified mg/kg	Rec. % (ave)
Be 9	He	1.6			0.2		
V 51	He	59.6			13.9		
Cr 52	He	191.9	187	103	88.8	90	99
Co 59	He	19.8	18.7	106	13.6	13.3	102
Ni 60	He	55.7	52.9	105	40.7	44.9	91
Cu 63	He	153.9	156	99	270.0	300	90
Zn 66	He	1031.6	970	106	825.1	919	90
As 75	He	44.7	44	102	3.2		
Se 78	H ₂	2.0			1.7		
Se 78	He	2.4			1.5		
Mo 95	He	1.3			6.9		
Ag 107	He	2.9			8.2		
Cd 114	He	8.5	8.07	105	1.7	1.84	90
Sn 118	He	0.02			36.0	40.8	88
Sb 121	He	1.6			2.8	3.05	92
Te 125	He	0.3			0.1		
Ba 135	He	828.3	817	101	319.2	367	87
Hg 201	He	4.1	3.83	107	3.2	3.11	102
Tl 203	He	1.1			0.1	0.14	
Pb 208	He	297.0	274	108	94.9	96	99

Table 4. Results of Replicate (n = 10) Analyses of Two Certified Reference Soil Samples (FeNeLab and BCR-144R)

Analyte	ORS mode	Low-level Measured spike conc. mg/kg			Rec.% (ave)	High-level Measured spike conc. mg/kg			
		mg/kg (ave, n = 10)	RSD (%)			mg/kg (ave, n = 10)	RSD (%)	Rec. % (ave)	
Be 9	He	1	0.8	3.5	81	800	773.9	3.6	97
V 51	He	50	50.9	4.0	102	800	771.4	2.5	96
Cr 52	He	150	149.6	4.0	100	1100	1062.7	2.5	97
Co 59	He	10	10.4	4.1	104	800	766.3	2.0	96
Ni 60	He	25	25.3	5.3	101	1100	1074.1	3.1	98
Cu 63	He	40	40.0	6.2	100	1100	1058.5	2.5	96
Zn 66	He	150	151.6	4.2	101	1100	1094.3	4.7	99
As 75	He	40	39.0	5.0	97	400	395.5	2.8	99
Se 78	H ₂	100	102.7	3.7	103	1300	1336.0	2.2	103
Mo 95	He	13	12.2	5.0	93	1300	1235.3	3.3	95
Ag 107	He	8	8.3	4.6	103	40	40.8	4.2	102
Cd 114	He	1.2	1.1	7.1	94	1100	1062.8	2.9	97
Sn 118	He	40	41.7	4.0	104	1300	1262.6	3.2	97
Sb 121	He	10	9.7	5.9	97	1300	1188.0	2.4	91
Te 125	He	80	82.1	4.2	103	750	807.4	2.4	108
Ba 135	He	120	121.1	4.5	101	1100	1102.2	5.6	100
Hg 201	He	0.4	0.4	4.4	106	13	13.5	4.3	104
Tl 203	He	23	24.0	4.6	104	40	41.3	3.4	103
Pb 208	He	100	101.9	4.7	102	800	778.1	4.0	97

Table 5. Results of Replicate (n = 10) Measurements Taken on 10 Nonconsecutive Days During a 30-Day Period of Both Low-Level and High-Level Spikes of Soil Samples

Analysis of Certified Reference Materials

Two certified reference materials (BCR-144R Domestic Sewage Sludge, IRMM, Belgium, and FeNeLab River Clay, FeNeLab, Netherlands) were analyzed in replicate as part of the validation procedure. The CRMs were prepared in the same manner as standard soil samples and measured on 10 different days during a 30-day time period. Table 4 shows the results of replicate (n = 10) analyses of both CRMs in mg/kg. Recoveries ranged from 87 to 108%, well within the regulatory requirement of 80 to 110%.

Determination of Precision and Accuracy at High and Low Concentrations

In addition to analysis of replicate CRMs, both low level and high-level spiked samples were analyzed in replicate (n = 10; 10 different days during 30-day time period) in order to determine both accuracy and precision over a wide range of concentrations (Table 5).

Sample Analysis

In order to test the long-term robustness of the HMI-equipped system, a 23-hour sequence consisting of an initial calibration and 235 soil samples was analyzed. Absolute drift was measured by monitoring the recovery of the five internal standards (⁶Li, Ge, Rh, In, Ir) in both gas modes (He and H₂) over the course of the sequence. Normalized recoveries (relative to the method blank) are shown in Figure 1. Overall downward drift over 23 hours was approximately 20%, which is easily corrected by internal standards and not sufficient to have a detrimental effect on method accuracy or sensitivity. By comparison, a similar system without HMI, running these samples directly would suffer severe loss of sensitivity (> 80%) due to cone clogging before the sequence was completed.

AS3000, like most methods used for regulatory compliance, requires ongoing calibration accuracy checks. In this case continuing calibration verification (CCV) samples (1 mg/kg As, 50 μ g/kg Hg, remaining elements 2 mg/kg) were analyzed after each 12 soil samples. Results are shown in Figure 2. Acceptable recoveries must be within \pm 10%. Ten percent control limits are shown in red, indicating that all CCV recoveries were well within the prescribed limits for the entire sequence. This excellent calibration stability not only ensures the most accurate sample results, but also eliminates time wasted in unnecessary recalibrations should a CCV fail during the sequence.

Productivity

The operation of the HMI accessory does not adversely affect productivity in any way, since the HMI conditions are constant throughout operation and do not require any additional

execution or stabilization time. Therefore, a given method run with HMI would take the same amount of time per sample as one run without HMI. HMI is also fully compatible with Agilent's time-saving pre-emptive and intelligent rinse functions, which minimize time wasted during both sample uptake and rinseout. Furthermore, since HMI permits the direct analysis of undiluted samples of many types, the extra time associated with either manual or autodilution is saved, which considerably shortens the total time (prep plus analysis) required per sample. The improved stability as a result of HMI use can also minimize the need for recalibrations and sample reruns, further reducing the average run-to-run time. In this work, the average run time for a sample in a 23-hour, 235-sample sequence of undiluted soil digestates was 5.9 minutes, including acquisition in both H₂ and He modes.

Conclusions

Based on Analytico's evaluation, when compared with conventional autodilution for high TDS, high acid digests of soil and sludge samples, Agilent's HMI interface provided a number of significant advantages.

- Speed – HMI does not require liquid dilution of sample and stabilization of diluted sample. It also permits the use of Agilent's pre-emptive rinse function, which allows rinsing of the sample tubing to begin before acquisition has finished.
- Low maintenance – There is no tubing to replace and no moving parts to maintain.
- Simple – There are no critical timing issues or plumbing common to continuous flow autodilutors.
- Flexibility – Since hardware changes or reconfigurations are not required after installation of HMI, the system can be switched between conventional mode and HMI mode on the fly.

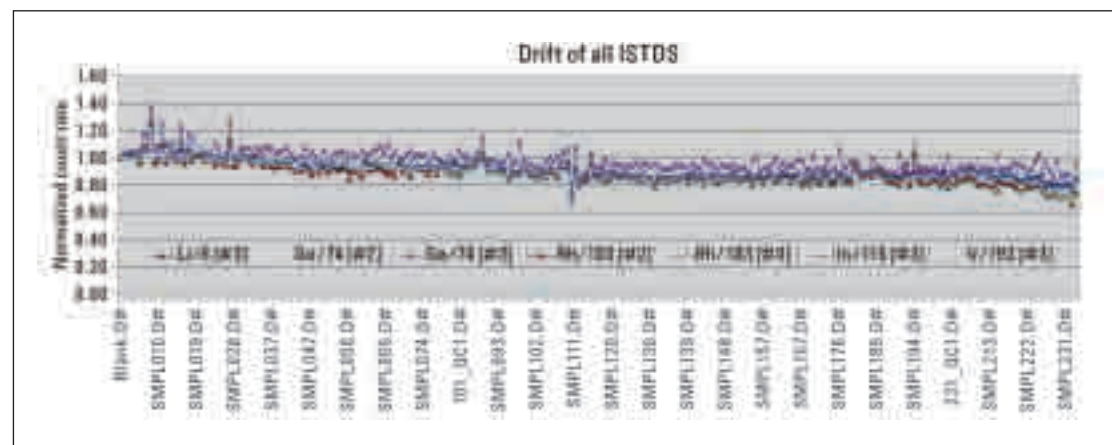


Figure 1. Normalized internal standard recovery in digested soil samples for the duration of the 23-hour sequence. Numbers next to each ISTD in the caption denote the ORS gas mode (#2 = H₂, #3 = He).

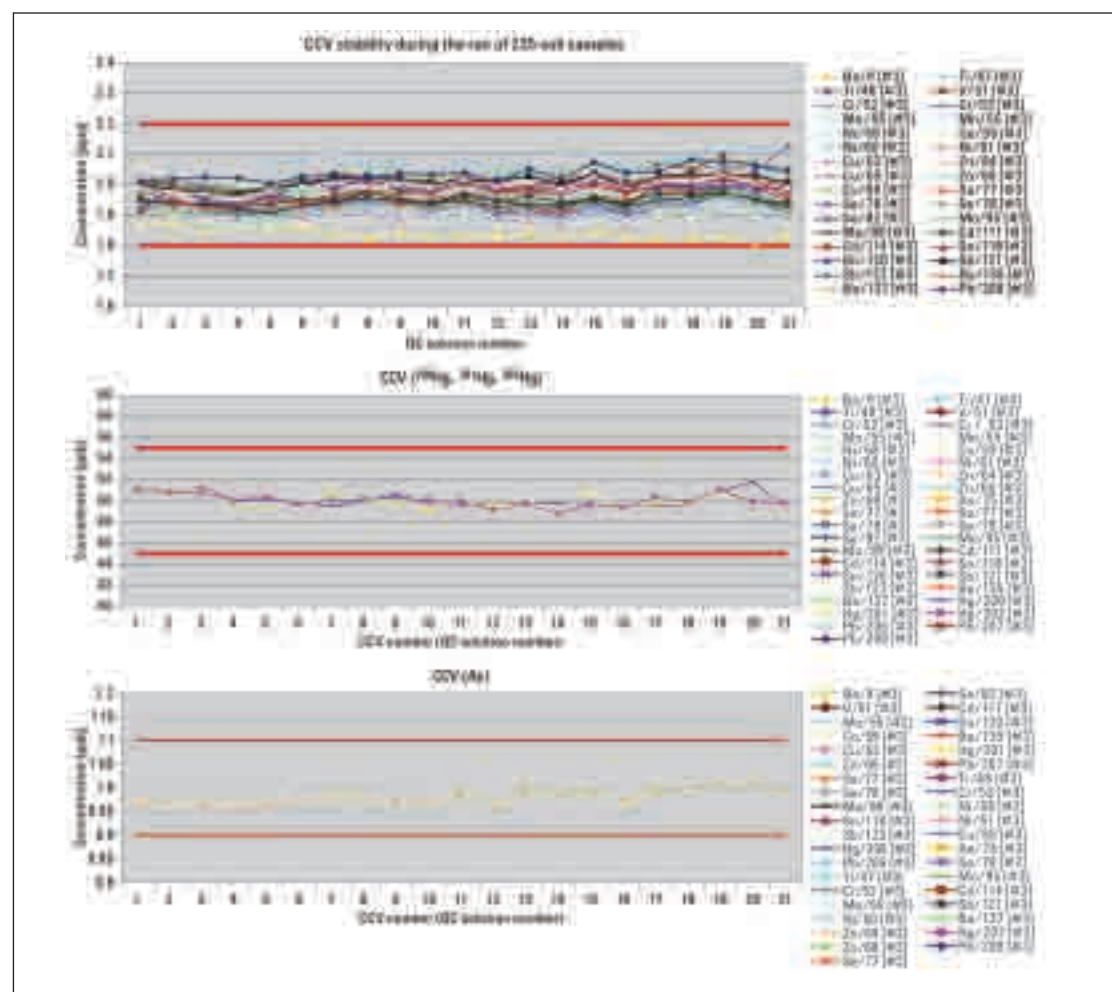


Figure 2. Continuing calibration check (CCV) recoveries (n=21) for all analyte elements over the 235-sample sequence of soils and sludges. Analytes at 2 mg/kg are shown on top, Hg, at 50 µg/kg in the middle, and As at 1 mg/kg at the bottom. Method required control limits (90 to 110%) are shown in red. Numbers after element names indicate ORS mode, #2 – H₂ mode, #3 – He mode.

These advantages have allowed Analytico to use a single 7500cx ICP-MS fitted with HMI to replace several instruments required for the analysis of these sample types, including conventional ICPMS, ICP-OES, and a dedicated mercury analyzer.

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REFERENCES

- 1 HMI theory and performance are discussed in detail in Agilent Product Overview: Performance Characteristics of the Agilent High Matrix Sample Introduction (HMI) Accessory for 7500 Series ICP-MS, 5989-7737EN.
- 2 MDLs calculated from 10 different days are for information only.