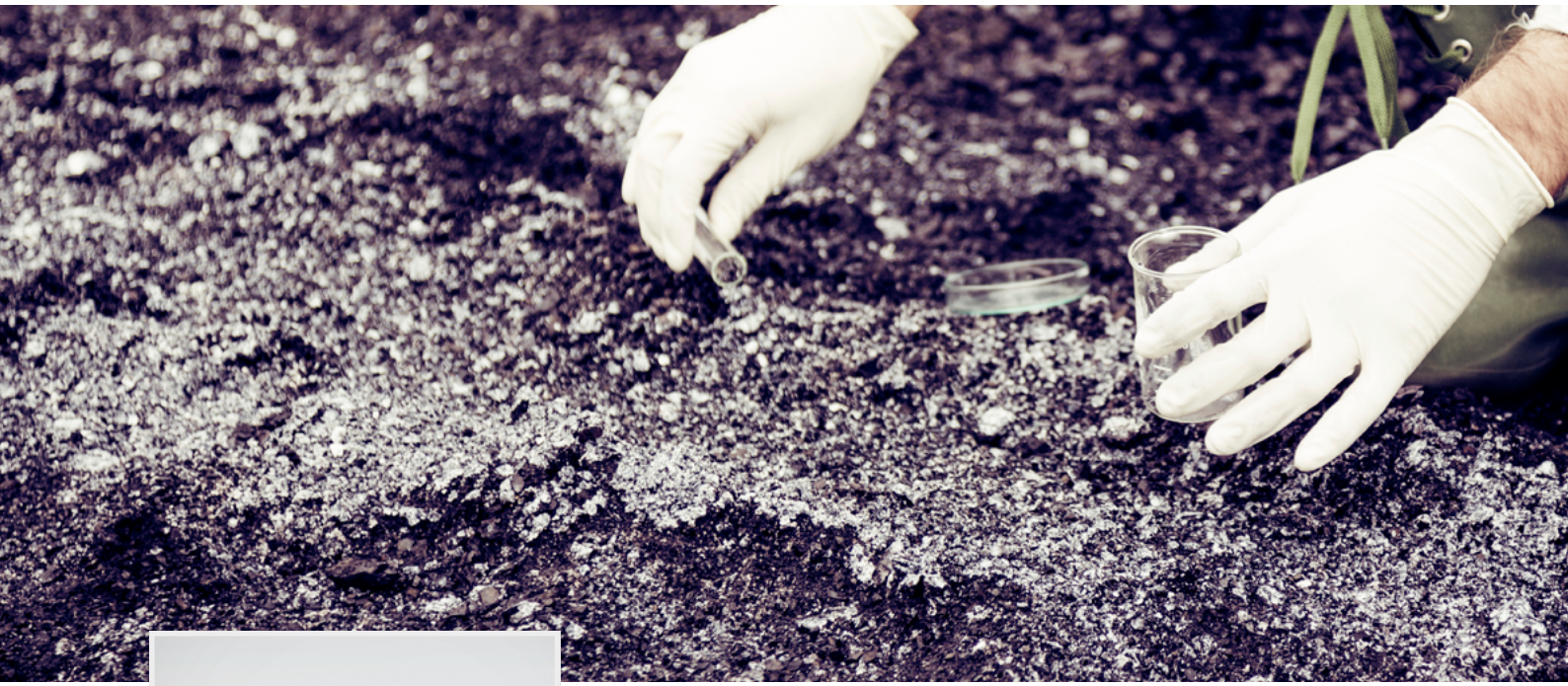

Challenge

Analysis of environmental samples with complex high matrix concentration and quantification of major, minor and trace elements

Solution

The PlasmaQuant MS provides reliable, precise and accurate results from trace to major elements concentration range.

Analysis of Marine Sediments and Sewage Sludge by PlasmaQuant MS

Introduction

To evaluate the potential ecotoxicology of soils, sediments an particularly sewage sludge constant monitoring for heavy metal content is required.The recycling of sewage sludge is closely linked to environmental regulations, so that a precise characterization is necessary. Industrial wastewater and waste are also subject to strict regulations and must be regularly checked and characterized. The determination of harmful and toxic elements in solid materials requires a digestion procedure prior to the analysis. Depending on sample type, matrix composition and the analyte elements of interest, the degree of difficulty of sample preparation varies. In this work, sample preparation was performed by microwave assisted acidic mineralization.

In total, 26 elements from major (percent), minor (ppm) and trace (ppb) levels were determined in three certified reference materials CRMs (two sewage sludge: BCR-144R and CRM055, one marine sediment: PACS-2). The obtained results clearly show excellent agreement with the certified values. Spike recoveries in the range of 90 to 104%, accuracy with Z-score uncertainty values ranging within -2.0 and +2.0 as well as precicion of less than 5% relative standard deviation (RSD) prove the method robustness and applicability to environmental samples.

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Materials and Methods

Instrumentation

All analytical work was performed using the PlasmaQuant MS featuring the integrated collision/reaction cell (iCRC) technology to remove polyatomic species formed in the plasma and the ReflexION ion optical system with 90° ion mirror for unique reflection of analyte ions that guarantees high sensitivity for improved precision and accuracy of all analyses. To detect the major, minor and trace element concentrations in a single run, the ADD, all digital detector, was used providing 11 orders of linear dynamic range without changing the detection mode and thus without the need for a frequent cross calibration. The ICP-MS system was coupled to an autosampler ASPQ 3300.

All experiments were carried out in a routine analytical laboratory, and not under 'clean room' conditions. Instrument operating conditions are summarized in Table 1, including the integrated Collision Reaction Cell (iCRC) modes using helium and hydrogen gases to remove problematic spectroscopic interferences on first-row transition metals.

Table 1: Instrument settings – PlasmaQuant MS

Parameter	Specification
Plasma gas flow	9.0 L/min
Auxiliary gas flow	1.10 L/min
Nebulizer gas flow	1.07 L/min
iCRC gas setting	No Gas for ^{7}Li, ^{9}Be, ^{59}Co, ^{66}Zn, ^{98}Mo, ^{107}Ag, $^{206+207+208}$Pb, ^{238}U He – 130 mL/min for ^{23}Na, ^{31}P, ^{24}Mg, ^{27}Al, ^{39}K, ^{44}Ca, ^{51}V, ^{52}Cr, ^{55}Mn, ^{60}Ni, ^{65}Cu, ^{86}Sr, ^{114}Cd and ^{205}Tl H2 – 120 mL/min for ^{33}S; ^{54}Fe, ^{75}As and ^{78}Se
Plasma RF power	1.20 kW
Dwell time	30 ms
Scan per replicate	25 (peak hopping, 1pt/peak)
No. of replicates	5
Pump rate	20 rpm – black/black PVC pump tubing (<1mL/min)
Torch	Fassel torch with 2.4mm injector
Cones	Ni-sampler and Ni-skimmer
Sampling depth	6.0 mm
Nebulizer type	MicroMist™ 0.4 mL/min (quartz concentric)
Ion optics	Auto-optimized
Spray chamber type	Quartz glass Scott-type with Peltier chiller
Spray chamber temperature	3 °C
Internal standards	Sc, Y, Ge, Rh, In, Ir, Tb and Bi, 5 µg/L, interpolate correction

Samples and Reagents

The following high purity reagents were used for all solution preparations:

- Deionized water (>18.2 MΩ*cm, Millipore MiliQ)
- Nitric acid Supra-quality 69 % (ROTIPURAN® Supra)
- Hydrochloric acid Supra–quality 35 % (ROTIPURAN® Supra)

Sample preparation

All three reference materials were digested in a microwave digestion system using the setting displayed in Table 2. After digestion samples were left to cool to ambient temperature, filled up to 50 mL using deionized water and filtered through a Whatman membrane prior to analysis. Afterward, all samples were diluted 100, 20 and 10 folds. Since all the samples had certified values, Z-score parameter was used to evaluate accuracy besides spike recovery efficiency.

$$Z - score = \frac{(x - \mu)}{\delta}$$

Where x represents the mean value obtained, $\boldsymbol{\mu}$ the reference value and $\boldsymbol{\delta}$ the uncertainty of the reference value.
Note: A Z-score indicates where the score lies on a normal distribution curve. A Z-score of zero describes a result that is exactly the average certified value, while a score of +3.0 describes a value that is much higher than average. Z-score between -2.0 and 2.0 is defined by a normal distribution of 97.72%.

Table 2: Digestion method parameters used by the microwave digestion system

Parameter	Specification
Sample amount	0.5 g dried and sieved
H_2O	2 mL
HNO_3	7.5 mL
HCl	2.5 mL
Vessel	PM60
Heating Stage 1 / time	140 °C / 5 min
Heating Stage 2 / time	175 °C / 5 min
Heating Stage 3 / time	210 °C / 20 min
Cooling / time	50 °C / 30 min
Final volume	50 mL with ultrapure H_2O filtered through Whatman N°.42 prior to analysis

Calibration

The method was calibrated with multi-element standards in the concentration levels of 0.5, 5, 25, 50, 250 and 500 µg/L for the minor elements Li, Be, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Tl, Pb and U and 0.5, 1, 2.5, 10, 25, 50 mg/L for P, S, Na, K, Al, Ca, Mg and Fe. All solutions were prepared in 50 mL plastic tubes from SARSTEDT using 1% HNO_3.
The calibration graphs in Figure 1 show good examples for the performance of the PlasmaQuant MS at defined concentrations levels. All calibrations were measured with correlation coefficients higher than 0.9999 in the range tested.

Evaluation

According to the expected interferences on certain mass/charge ratios, different isotopes were measured by using collision gas (He) or a reactive gas (H2) by utilizing the iCRC technology of Analytik Jena. Therefore, for each measurement, three condition sets (Helium, no Gas and Hydrogen modes) were prepared with the respective isotopes in the appropriate set (see Table 3). Within one measurement, all condition sets were executed with switching times of 30 seconds. For data recording, five average values were calculated from twenty-five scans each, which were used for the calculation of one average value including standard deviation.

Table 3: Expected interferences and used iCRC gases

Isotope	Expected interference	iCRC mode
^{7}Li	-	No gas
^{9}Be	-	No gas
^{23}Na	-	He (due to high concentration/signal)
^{24}Mg	-	He (due to high concentration/signal)
^{27}Al	$^{11}B^{16}O$	He
^{31}P	$^{15}N^{16}O$	He
^{33}S	$^{17}O^{16}O$	H_2
^{39}K	$^{23}Na^{16}O$	He
^{44}Ca	$^{28}Si^{16}O$	He
^{51}V	$^{35}Cl^{16}O$	He
^{52}Cr	$^{36}S^{16}O$; $^{36}Ar^{16}O$; $^{40}Ar^{12}C$	He
^{54}Fe	$^{38}Ar^{16}O$	H_2
^{55}Mn	$^{39}K^{16}O$	He
^{59}Co	-	No gas
^{60}Ni	$^{44}Ca^{16}O$	He
^{65}Cu	$^{49}Ti^{16}O$	He
^{66}Zn	-	No gas
^{75}As	$^{40}Ar^{35}Cl$	H_2
^{78}Se	$^{40}Ar^{38}Ar$	H_2
^{86}Sr	-	He (due to high concentration/signal)
^{98}Mo	-	No gas
^{107}Ag	-	No gas
^{114}Cd	$^{98}Mo^{16}O$	He
^{205}Tl	-	He (due to high concentration/signal)
$^{206+207+208}Pb$	-	No gas
^{238}U	-	No gas

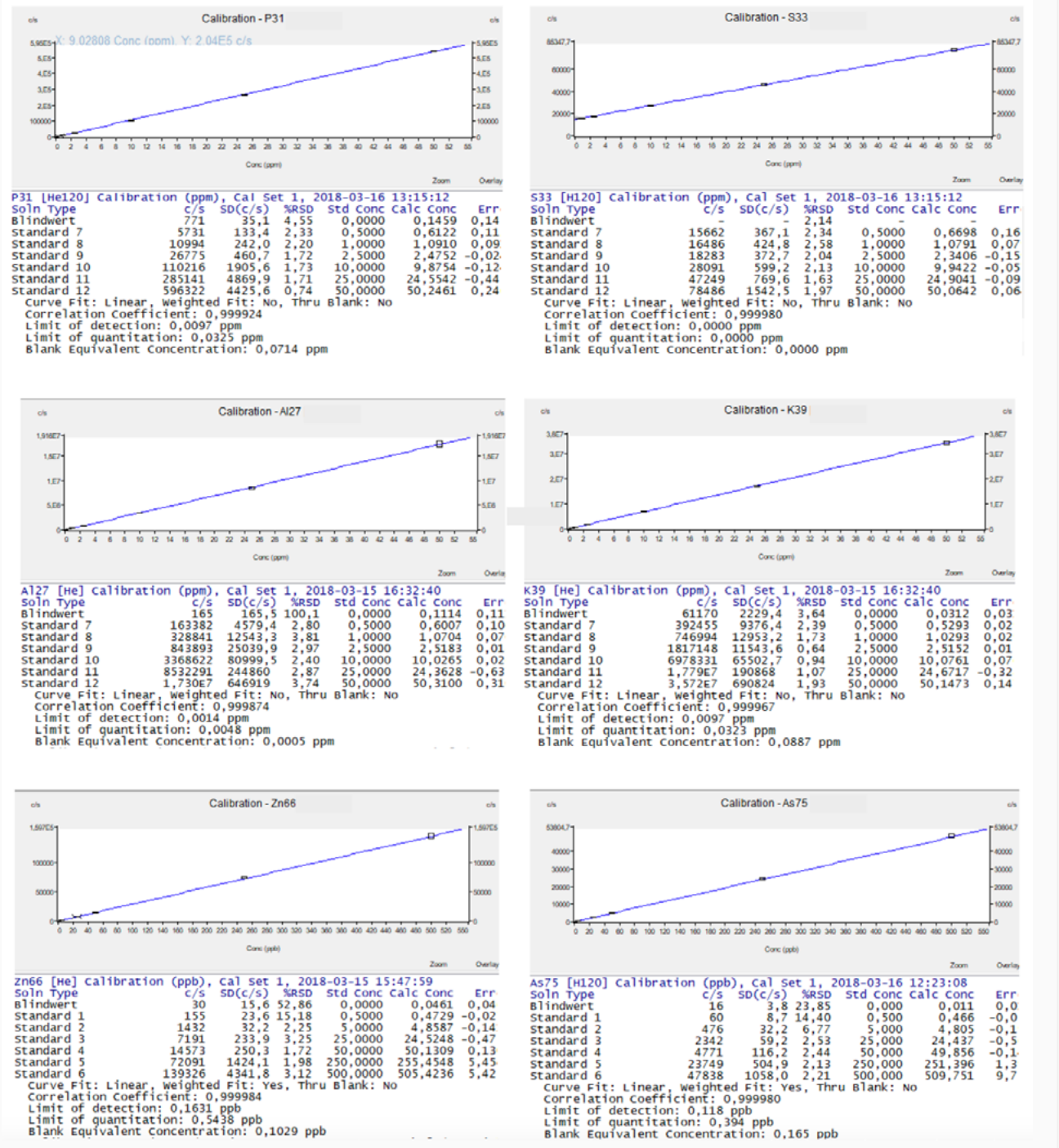

Figure 1: Calibration graphs for some major and minor elements investigated

Result and discussion

Tables 4, 5 and 6 present results achieved in BRC-144R (sewage sludge), CRM055 (sewage sludge 4) and PACS-2 (marine sediment) respectively. Mean values of the different dilution performed, standard deviation (%RSD), recoveries rates (%REC) and Z-score are listed.

Table 4: Results of BCR-144R, sewage sludge

Isotope	Certified value [mg/kg]	Uncertainty [mg/kg]	Mean value [mg/kg]	stdev [mg/kg]	RSD [%]	Recovery [%]	Z-score
^{52}Cr	104	3	98.7	0.7	0.7	95	-1.8
^{55}Mn	208	3	210	2.5	1.2	101	0.7
^{59}Co	15	0.6	14.2	0.7	4.9	95	-1.3
^{60}Ni	47.7	1.1	49.0	0.6	1.1	103	1.2
^{65}Cu	308	7	301	7.1	2.4	98	-1.0
^{66}Zn	932	23	912	23	2.5	98	-0.9
^{114}Cd	1.82	0.10	1.83	0.12	6.6	100	0.0
$^{206+207+208}$Pb	106	1.6	103	4.4	4.3	97	-1.9

Table 5: Results of CRM055, sewage sludge 4

Isotope	Certified value [mg/kg]	Uncertainty [mg/kg]	Mean value [mg/kg]	stdev [mg/kg]	RSD [%]	Recovery [%]	Z-score
^{23}Na	774	198	954	25.5	2.7	123	0.9
^{31}P	22000	6370	21175	1255	5.9	96	-0.1
^{33}S	10900	4030	14785	49.5	0.3	136	1.0
^{24}Mg	9180	2640	11221	165	1.5	122	0.8
^{27}Al	15300	3390	17825	213	1.2	117	0.7
^{39}K	2460	410	2866	31.2	1.1	117	1.0
^{44}Ca	47400	13000	52957	930	1.8	112	0.4
^{52}Cr	288	36.7	336	4.1	1.2	117	1.3
^{54}Fe	19000	9930	24416	163	0.7	129	0.5
^{55}Mn	667	121	685	14.5	2.1	103	0.2
^{59}Co	95.5	7.88	112	3.3	2.9	118	0.8
^{60}Ni	163	16.3	177	4.5	2.5	109	0.9
^{65}Cu	482	59.6	487	16.8	3.4	101	0.1
^{66}Zn	1250	253	1294	36.7	2.8	104	0.2
^{75}As	236	28.1	257	8.5	3.3	109	0.7
^{98}Mo	131	34.9	147	3.6	2.5	113	0.5
^{114}Cd	60.6	4.13	60.0	1.1	1.8	99	-0.1
$^{206+207+208}$Pb	154	14.2	161	2.3	1.4	104	0.5

Table 6: Results of PACS-2, marine sediment

Isotope	Certified value [mg/kg]	Uncertainty [mg/kg]	Mean value [mg/kg]	stdev [mg/kg]	RSD [%]	Recovery [%]	Z-score
^{7}Li	32.2	2.0	30.1	2.2	7.3	93	-1.1
^{9}Be	1.0	0.2	0.90	0.1	5.6	90	-0.5
^{51}V	133	5	130	3.5	2.7	98	-0.5
^{52}Cr	90.7	4.6	84.0	1.0	1.2	93	-1.5
^{55}Mn	440	19	421	2.4	0.6	96	-1.0
^{59}Co	11.5	0.3	11.2	0.2	1.8	97	-1.1
^{60}Ni	39.5	2.3	40.2	0.6	1.6	102	0.3
^{65}Cu	310	12	313	0.9	0.3	101	0.2
^{66}Zn	364	23	347	20	5.7	95	-0.7
^{75}As	26.2	1.5	25.5	1.3	5.1	97	-0.5
^{78}Se	0.92	0.22	0.94	0.09	9.3	102	0.1
^{86}Sr	276	30	265	1.5	0.6	96	-0.4
^{107}Ag	1.22	0.14	1.27	0.1	7.8	104	0.4
^{114}Cd	2.11	0.15	2.06	0.12	5.8	97	-0.4
^{205}Tl	0.6	-	0.58	0.04	6.8	97	-
$^{206+207+208}$Pb	183	8	189	1.3	0.7	103	0.7

Accuracy

Certified reference materials were measured in order to evaluate the accuracy of the method. The Z-score parameter was used to evaluate accuracy besides spike recovery efficiency. All certified elements were within the certified control ranges (-2.0 < Z-score < 2.0) (Figure 2). Due to the high sensitivity and robustness the PlasmaQuant MS was able to detect trace and major concentrations in a single method run and is a highly suitable instrument for the determination of trace and major elements in all types of samples.

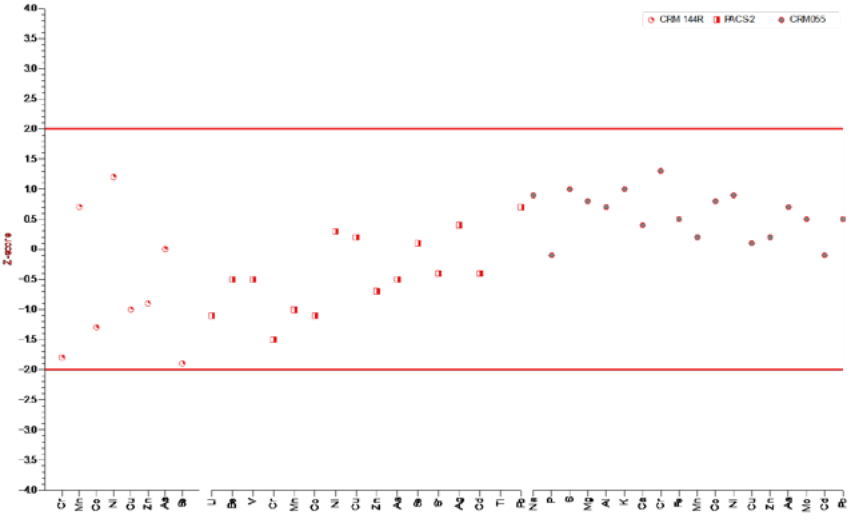

Figure 2: Z-score distribution of all elements measured in three CRMs

Precision

The relative standard deviation (RSD) was used as a parameter to assess the precision of the measurements. On average RSDs of 2.8% were achieved. Precision and accuracy (recoveries rates) of the three CRMs are shown in Figure 3. It can be seen that all recovery rates are within 80 to 120%, except for Na, S, Mg and Fe in CRM055 due to higher uncertainty of the reference value (Z-score for those elements where <1.0) while the RSDs are < 5%. Except for some elements such as Li, Se and Ag in PACS-2 which are within 8 to 9%. All results within the range of ppb to % showed great precision and accuracy with the methodology applied during all the measurements.

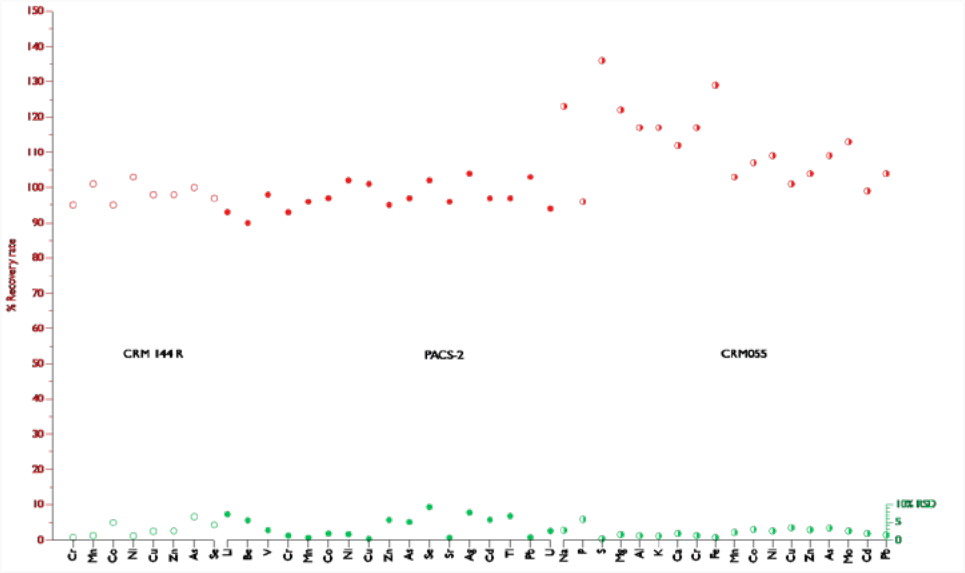

Figure 3: Recovery rate and precision of three CRMs. All measurements are within the range specified.

Conclusion

The PlasmaQuant MS offers a simple, fast, and cost-efficient method for the analysis of soils and sewage sludge. The instrument behaves as a robust instrument able to run different matrices in the same sequence using the same calibration curve without the need of preparing different methods. In summary, the actual method is highly suitable for the determination of trace and major elements in complex environmental sample types such as soil, sediment ad sewage sludge. The PlasmaQuant MS includes several innovative technologies (Eco Plasma, ReflexION ion mirror, iCRC, pre-quadrupole, alldigital detector) that provide advantages especially for the determination of complex matrix samples.

- Excellent sensitivity on the whole mass range for the lowest limits of detection.
- Excellent plasma robustness for all matrices with the new RF generator using only half the Ar consumption (<11 L/min).
- The iCRC (integrated Collision Reaction Cell) combines collision and reaction modes to correct efficiently for the spectral interferences.
- Ease of use of the instrument with simplified maintenance operations and the user-friendly software ASpect MS.

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