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Determination of Al, Ca, Fe, K, Mg, P and Na in soil by ICP-AES and method validation of the AL-method

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Bachelor Degree project in Chemistry (15 hp)

Abstract

Concentrations of Al, Ca, Fe, K, Mg, P and Na are determined in soil. The soil is prepared by an open vessel extraction by ammonium lactate and acetic acid, AL-method. The extraction is a soft extraction thus the concentrations determined are not total concentrations but the concentrations of the elements which plants have access to. The AL-method is designed for agriculture hence the reason for measuring a concentration that is not the total concentration of the elements in the soil. For the sample preparation 5.00 gram of soil is leached with 100.0 mL AL-solution, the sample is shaken and filtered before it is analysed by ICP-AES.

A validation of the AL-method is done were the LOD, LOQ, linearity, robustness, trueness, precision and day-to-day variation is determined. LOD and LOQ were determined by several measurements on blank solutions. Since the concentrations in the blank solutions and the concentration of Na were lower than LOD and LOQ, the concentrations are less accurate determined. The linearity of the instrument was controlled to confirm that neither samples, including the spiked samples with 50 % extra, nor calibration solutions exceeds the linear range. The robustness proved the method to be sensitive for changes in the amount of soil used for the preparation and for changes in the concentration of the AL-solution. The trueness of the method is determined by calculating the recovery for spiked samples and blanks. The recovery for the blanks was around 100 % for most of the elements, for the samples however, the recovery was lower probably due to re-adsorption of the metals back on the soil particles, as the equilibrium change when more metals are added in the solution. The precision of the method was determined by the RSD of samples made on the same day. A majority of the elements had a RSD lower than 2 %. Day-to-day variation of the method was determined with a one way ANOVA for all elements. The method showed a significant day-to-day variation for all elements.

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Abbreviations

LOD	Limit of Detection
LOQ	Limit of Quantification
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
AL-method	Ammonium-Lactate-method
RSD	Relative Standard Deviation
CRM	Certified Reference Material
rpm	Rounds Per Minute
MV	Mean value of Variance
VM	Variance of Mean value
ANOVA	Analysis Of Variance

Introduction

There are various different elements in the ground. In this study aluminium, calcium, iron, phosphorus, magnesium, potassium and sodium concentration in soil are determined after extraction with the AL-method and analysis by ICP-AES. The AL-method [1] is an open vessel extraction where the sample is extracted with ammonium lactate and acetic acid; it is commonly used for preparation of soil samples for analysis. Extraction by ammonium lactate and acetic acid is a soft extraction.

This study is done at Agrilab AB, which is a company that analyse soil, cattle food and manure for agriculture and individuals sending samples to Agrilab.

This method is designed to measure the concentrations of the elements that are easily accessible to the plants; hence it does not provide the total concentrations of the elements in the soil. The purpose of the analysis method is for agriculture and the information needed there is how much of the elements that are accessible for the plants growing. Due to this, only the easily accessible metals are measured, hence the soft extraction is used. In order to measure the total concentrations in the soil stronger acids would need to be used for the digestion. [2]

The principle of the AL-method is to extract the elements of interest from the soil to the water phase with the ammonium lactate and acetic acid. Then the soil is filtered away and the concentrations of the different metals are measured in the water phase with ICP. The reason that the soil is filtered away is because it can damage the ICP-instrument and influence the results. [2]

The plants growing in the soil needs potassium for some essential functions in the plant, one of them is for transport of water, carbohydrates and nutrients in the plant. [3] A phosphorus deficiency can lead to inhibition of the plant growth. [4] Magnesium plays an important part for cell membranes and cell walls in the plants, it is also important for many enzymes which are essential for the plant. [5]

Since P, K, Ca and Mg all are essential elements for the plants; knowing the amount of elements in the soil is important. [6] It is the only way for the plant to get access to the elements. It is important that the plants can grow because they fed humans and to get the maximum of the plants required amounts of essential elements are needed. With the knowledge of the concentrations in the ground right amounts of fertilizers can be used which can save both time and money for the farmers. Over fertilization (eutrophication) is a problem as a result of a too high usage of P and N in fertilizers. It affects both animals and marine life negatively. Phosphorus in lakes lead to an increase of algae, which reduce the

oxygen levels thereby killing fishes in the lakes. [6] Calcium ions are important for enzymes and for transport of nutrients over cell membranes. [7]

It is important that eutrophication is avoided since it damages the environment while the plants still get enough of these essential elements to grow in a rapid speed. It is therefore of importance to know the amounts of elements in the soil.

The goal of the study was to determine the amount of Al, Ca, Fe, K, Mg, P and Na in soil prepared with the AL-method and analysed with ICP-AES. In addition to the concentration determination the method is validated.

Material and method

Sample preparation

First 1.5 litres of lactic acid (90%) was diluted to 4.5 litres with deionized water and put into a warming cupboard at 96-98 °C for two days. After the two days the solution is cooled in a water bath. 20.27 g 98.6 % NaOH is dissolved in 519.81 g of water giving a solution of 1.000 M NaOH. 0.10 g phenolphthalein is dissolved in 100 mL 95 % ethanol.

After the hydration 1 mL of the lactic acid solution was titrated with the sodium hydroxide solution and the molality is calculated for the lactic acid. 4.99 g of lactic acid were titrated with 21.93 g 1.000 M NaOH giving the lactic acid solution a concentration of 4.22 moles/kg. The acetic acid was also titrated with the sodium hydroxide solution. 3.15 g acetic acid was titrated with 54.75 g 1.000 M NaOH; the acetic acid solution has the measured concentration of 16.71 moles/kg.

The stock AL-solution is then made by mixing 392.07 g 98.3 % ammonium acetate, 897.81 g acetic acid and 1183.60 g lactic acid and then diluting to 5 litres with distillate water. The final solution is 1 M ammonium lactate and 4 M acetic acid, before usage the solution is diluted 10 times and the pH of the diluted solution should be 3.75 ±0.05.

5.00 grams of soil is weighed up and in a tube and 100.0 ml of AL-solutions is added. For all samples the standard soil from Agrilab is used. The sample is then shaken for 90 minutes. When the samples are shaken the soil is filtered away with Munktells filter paper OOH, 150 mm. The first 2-5 mL of the filtered liquid is not used due to having a higher risk of containing contaminations from the filter paper. After the first mL of liquid has passed a test tube is filled with sample for analysis by ICP-AES.

Calibration solution

Calibration solutions were prepared with the concentrations in table 1. Before and after each set of samples is measured the concentration of a control solution is measured. The

purpose of the control solution is to adjust the determined concentration of the samples by the same amount as the different between the determined and known concentration of the control solution [4].

Table 1. Concentrations for the calibration solutions and the control solution.

Solution	Al (mg/L)	Ca (mg/L)	Fe (mg/L)	K (mg/L)	Mg (mg/L)	P (mg/L)	Na (mg/L)
0%	0	0	0	0	0	0	0
100%	50.00	500.00	100.00	100.00	100.00	100.00	30.00
Control solution	5.00	50.0	10.0	10.0	10.0	10.0	3.0

The control solution is used to adjust the concentration measured on the sample according to the bias measured on the control solution. The metal solutions used to make the calibration solutions are found in table 2.

Table 2. The solutions used to prepare calibration solutions and the linearity control solutions.

Element	Solution	Source
Al	Spectrascan SS-10512	Al metal
Ca	Spectrascan SS-10506	CaO
Fe	Spectrascan SS-10504	Fe metal
K	Spectrascan SS-10507	KNO_3
Mg	Spectrascan SS-10540	Mg metal
P	Spectrascan SS-10244	H_3PO_4
Na	Spectrosol Prod 14148	$NaNO_3$

Instrument and settings

The instrument used for analysis was a Spectroblue_SOP (Standard Operating System) ICP instrument, setting for the instrument used for the analysis found in table 2. The spray chamber used was; Spectro Spray Chamber Scott AD36/DURAN P/N 48105078 and the nebulizer used was, Spectro Zerstäuber Cross-Flow Standard P/N 75060502.

Table 3. Settings used for the ICP machine.

Plasma Power	1450 W
Pump Speed	30 rpm
Coolant Flow	14.00 L/min
Auxiliary Flow	1.00 L/min
Nebulizer Flow	0.75 L/min

These settings are the standard for the ICP and are not optimized for the samples measured. Figure 1 is a picture taken on the ICP showing the different flows described in table 3.

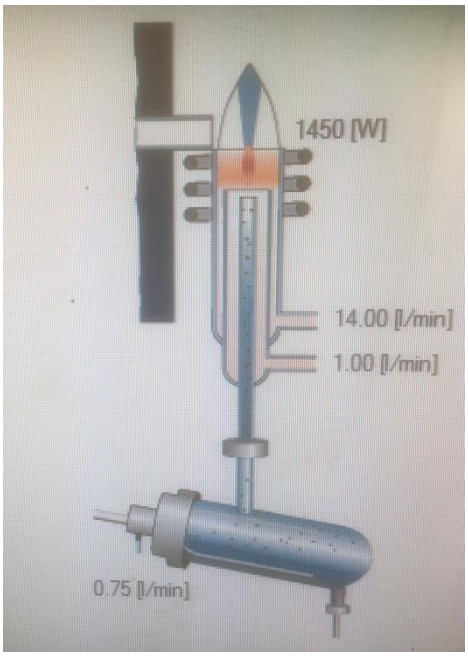

Figure 1. The figure shows the directions of the different flows and how the samples reach the plasma.

The concentrations of Al, Ca, Fe, K, P, Mg and Na in the soil samples are measured with ICP-AES. The wavelengths at which the elements are measured are listed in table 4.

Table 4. The wavelengths at which the elements are measured at for every measurement.

Element	Wavelength (nm)
Al	176.641
Ca	183.801
Fe	259.941
K	766.491
Mg	279.079
P	177.495
Na	589.592

The wavelengths used are the standard wavelengths used at Agrilab for this analysis.

Setup for the validation of the method

Parameters to be determined in the study are total amounts of the different elements as well as linearity, LOD, LOQ, trueness, precision, robustness and day-to-day variation of the method. All of these parameters are used for the validation of the method. Different tests and calculations will be done to control the parameters.

Linear range

The linear range of the instrument is determined by measuring solutions of concentrations from 0.1 % to 200 % of the standard sample concentration. The concentration ranges

corresponds to concentrations between 0.05 mg/L to 200 mg/L for Al, Fe, Mg, P and K, between 0.5 mg/L to 1000mg/L for Ca and between 0.03 and 60 mg/L for Na. The linearity is the range in which the signal to concentration is linear. The linear range is controlled to confirm that no samples have a concentration above of the linear range. Concentration measured above of the linear range will be lower due to saturation of analyte outside of the linear range. Linearity is accepted if the correlation factor R^2>0.999 for the curve. For the trueness where the samples are spiked with extra metals there is very important to know that the samples still are within the linear range with the extra metals added, therefore the linear range must be tested beyond the sample concentrations.

LOD and LOQ

The limit of detection of the method is determined by 2 measurements on 6 blank solutions. From the measurements of the blanks the standard deviation is calculated. LOD of the method is calculated by $3 * \frac{s}{slope}$ and LOQ of the method is calculated in a similar way, $10 * \frac{s}{slope}$. Where *s* is the standard deviation for the intensity of the blank and the slope is the slope for the calibrations curve.

Trueness

Systematic errors lead to a bias in the method, which affect the trueness of the method, as trueness is the lack of a bias for a method. To determine the trueness of the method, samples and blanks are spiked with a known amount of analyte and thereafter the recovery of the added spike is calculated and will be used to determine the trueness of the method. The recovery is calculated by dividing the concentration calculated from the signal from the spike with the known amount of added spike. The trueness is measured on 14 samples and 10 blanks.

One other way to determine the trueness of is to use a certified reference material (CRM) with a known concentration and use the same sample procedure as for the normal samples. The problem is that the method is not designed to measure total concentration, which is the concentration that is given for the CRM samples. Thus the measured value will be lower than the reference value and no useful information would be gained. Therefore only spiked samples will be used to determine the trueness of the method.

Precision

Precision is defined as the random errors of a method. [8] With low random errors the repeatability of the method will be good. The repeatability is determined by the relative standard deviation. RSD will be calculated from the standard deviations of samples made on the same day. RSD is calculated by 100*s/x, where *s* is the standard deviation and x is the mean value. The reason the RSD in calculated from samples made on the same day is because day-to-day variation should not be included in the determination of RSD. A low value of RSD indicates that the difference between the samples measured on the same day

is low. With a low difference between the samples made on the same day, the preparation and analysis is precise.

RSD was also calculated on samples analysed on different days. One sample for each day for the 5 days was used for the calculation. The value of the RSD for different days will give an indication of the reproducibility of the method.

Robustness

The robustness of the method is a parameter that determines how sensitive the method it is to small changes. If the method is very sensitive it is more difficult to get repeatability of the results. It will be tested in two different ways, the first by adding 20% more and 20% less soil in the samples. The second test for the method is to dilute the stock AL-solution 20% more and 20% less to get two different concentrations of the AL-solution.

Six samples with the different preparation methods were made on two different days for a total of 12 unique samples. The results from those samples are compared to the results of the standard method.

To determine whether there is a difference between these results and the results from the normal samples a two-sided t-test will be used for the results from the samples with the special preparation methods against the normal samples. [8] If the value is lower than the critical value for the test there is no difference, however if the value is larger than the critical value, there is a proven difference between the results. A significant difference purposes that the method is sensitive for changes in the preparation of the samples.

Day to day variation

Eight samples will be made and measured every day for five days and the eventual day-to-day variation of those samples will be tested by a one-way ANOVA. [8] The ANOVA is a comparison of the variances and mean values for sample done on different days.

Results and discussion

A total of 46 standard samples were done and analysed in addition to samples with alternative preparation methods see robustness. The standard deviation, relative standard deviation and day-to-day variation were calculated with the standard samples. All concentrations are mean values of two measurements for both standard samples and robustness samples.

The concentrations of the samples are calculated by the concentrations given from the measurements. The ICP program give the concentrations in mg/L, by multiplying the value with the volume and dividing it by the added amount of soil the units is converted to mg/g. Before and after the samples are measured a control solution with concentration, see table

5, is measured. The quotient for the known control solutions concentration and the measured concentration is used to adjust the calculated values of the samples for the bias in the measured concentration.

Data from all the measurements are found in the appendix.

Table 5. Results for the standard samples.

Sample	Al (mg/g)	Ca (mg/g)	Fe (mg/g)	K (mg/g)	Mg (mg/g)	P (mg/g)	Na (mg/g)
1 day 1	0.189	7.58	1.28	0.256	0.203	0.363	0.018
2 day 1	0.186	7.53	1.23	0.255	0.202	0.357	0.016
3 day 1	0.187	7.61	1.26	0.258	0.202	0.360	0.034
4 day 1	0.186	7.56	1.24	0.256	0.201	0.357	0.019
5 day 1	0.190	7.65	1.31	0.258	0.207	0.364	0.019
6 day 1	0.184	7.49	1.26	0.253	0.201	0.361	0.016
7 day 1	0.188	7.53	1.28	0.255	0.203	0.363	0.019
8 day1	0.189	7.59	1.26	0.259	0.203	0.366	0.024
1 day 2	0.193	7.60	1.28	0.261	0.207	0.360	0.021
2 day 2	0.196	7.60	1.28	0.261	0.207	0.361	0.024
3 day 2	0.192	7.63	1.25	0.257	0.205	0.360	0.025
4 day 2	0.193	7.58	1.24	0.259	0.205	0.361	0.029
5 day 2	0.191	7.56	1.25	0.253	0.202	0.358	0.029
6 day 2	0.192	7.58	1.25	0.259	0.204	0.361	0.026
7 day 2	0.190	7.52	1.23	0.255	0.203	0.356	0.031
8 day 2	0.192	7.68	1.25	0.257	0.206	0.364	0.027
1 day 3	0.182	7.57	1.26	0.253	0.197	0.351	0.021
2 day 3	0.182	7.50	1.27	0.251	0.201	0.354	0.023
3 day 3	0.178	7.57	1.27	0.250	0.197	0.358	0.018
4 day 3	0.180	7.56	1.29	0.253	0.197	0.351	0.018
5 day 3	0.178	7.63	1.26	0.251	0.198	0.356	0.018
6 day 3	0.181	7.41	1.26	0.252	0.197	0.353	0.018
7 day 3	0.179	7.55	1.27	0.250	0.196	0.358	0.018
8 day 3	0.178	7.55	1.28	0.249	0.197	0.355	0.018
1 day 4	0.185	7.48	1.24	0.256	0.207	0.356	0.026
2 day 4	0.189	7.63	1.26	0.258	0.209	0.368	0.025
3 day 4	0.185	7.47	1.23	0.257	0.207	0.356	0.031
4 day 4	0.189	7.68	1.26	0.257	0.207	0.353	0.035
5 day 4	0.184	7.44	1.23	0.254	0.205	0.357	0.032
6 day 4	0.189	7.60	1.24	0.262	0.211	0.362	0.035
7 day 4	0.180	7.57	1.21	0.252	0.203	0.351	0.025
8 day 4	0.187	7.57	1.24	0.261	0.208	0.363	0.025
1 day 6	0.179	7.35	1.18	0.244	0.193	0.348	0.016

2 day 6	0.180	7.38	1.17	0.243	0.193	0.347	0.016
3 day 6	0.179	7.42	1.18	0.243	0.193	0.349	0.016
4 day 6	0.180	7.29	1.16	0.243	0.193	0.344	0.017
5 day 6	0.193	7.40	1.18	0.250	0.195	0.347	0.018
6 day 6	0.180	7.35	1.16	0.245	0.193	0.344	0.016
7 day 6	0.179	7.33	1.16	0.243	0.192	0.346	0.016
8 day 6	0.182	7.33	1.17	0.243	0.194	0.345	0.017
9 day 6	0.182	7.35	1.17	0.244	0.194	0.350	0.016
10 day 6	0.197	7.34	1.18	0.255	0.195	0.346	0.019
11 day 6	0.187	7.36	1.16	0.250	0.195	0.353	0.018
12 day 6	0.182	7.42	1.17	0.245	0.194	0.349	0.017
13 day 6	0.181	7.37	1.16	0.244	0.193	0.346	0.017
14 day 6	0.186	7.40	1.18	0.247	0.195	0.355	0.018

Mean value for the elements are calculated for all the determined values. From the mean values and confidence intervals, the concentration of the elements in the soil is determined. See table 6 for the determined concentrations of the metals.

Table 6. Concentration of the different metals in the soil examined.

Element	Al	Ca	Fe	K	Mg	P	Na
Concentration (mg/g)	0.185 ± 0.002	7.50 ± 0.03	1.23 ± 0.01	0.252 ± 0.002	0.200 ± 0.002	0.355 ± 0.002	0.022 ± 0.002

Linear range

To determine the linear range eight solutions were prepared. First the solution containing 200 % of the expected sample concentration from measurements done earlier at the lab was prepared. The other solutions were made from the 200 % solution. Concentrations of the linearity solutions are found in table 7.

Table 7. Concentrations of the elements in all of the eight linearity solutions.

Solution	Ca (mg/L)	Al (mg/L)	Fe (mg/L)	K (mg/L)	Mg (mg/L)	P (mg/L)	Na (mg/L)
200%	1000.00	100.00	200.00	200.00	200.00	200.00	60
100%	500.00	50.00	100.00	100.00	100.00	100.00	30
50%	250.00	25.00	50.00	50.00	50.00	50.00	15
10%	50.00	5.00	10.00	10.00	10.00	10.00	3.0
5%	25.00	2.500	5.000	5.000	5.000	5.000	1.5
1%	5.000	0.500	1.000	1.000	1.000	1.000	0.30
0.5%	2.500	0.250	0.500	0.500	0.500	0.500	0.15
0.1%	0.500	0.050	0.010	0.010	0.010	0.010	0.03

All solutions were measured and the intensity of each element is plotted against the concentration of the respective element. Assuming all the concentrations are within the linear range all plots should have a R^2 >0.999. If the correlation factor is lower the plots will be investigated further to see which solutions that might be outside the linear range. The slope, intercept, correlation factor and concentration range for all solutions are found in table 8.

Table 8. Slope, intercept, correlation factor and concentration range for all solutions used to determine the linear range.

	Al	Ca	Fe	K	Mg	P	Na
Slope	5814.6	6885.7	47619	4824.6	3970.2	10298	40584
Intercept	1430.6	23346	46007	-275.35	1824.4	9266.4	4214.2
Correlation factor	0.999665	0.999735	0.999377	0.999987	0.999868	0.999314	0.999866
Concentration range (mg/L)	0 - 100	0 - 1000	0 - 200	0 - 200	0 - 200	0 - 200	0 - 60

The best and worse graphs are shown in figure 2 as examples.

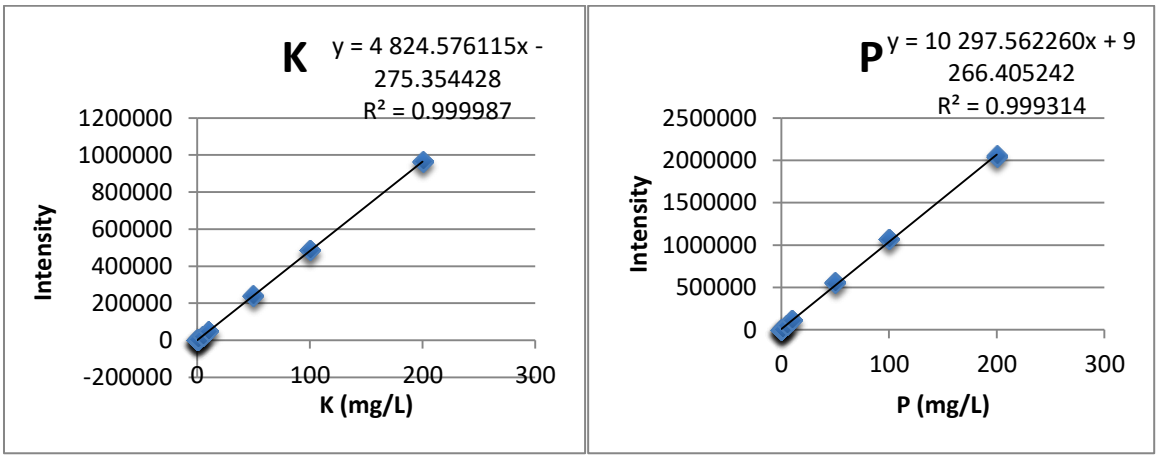

Figure 2. The two linearity curves with best and worse correlation factor.

The elements are measured at different concentrations for the linearity because there are different amounts of the elements in the soil and therefor the calibrations solutions and linearity test have to be in corresponding concentrations. The linearity was tested with solutions from 0.1 % to 200 % of the expected concentrations from the samples and for these concentrations the instrument is linear for all the elements. The instrument is therefore linear over the entire range were the samples have their expected concentrations.

The trueness is tested by spiking samples with 50 % extra of the sample concentration of all the elements and therefore it is important that the instrument is linear for the wavelengths used even for the spiked samples.

LOD and LOQ

Limit of detection and quantification are determined by measurements on 6 different blank solutions prepared from the same solution. For the LOD and LOQ the intensities are used in addition to the slopes of the calibration curves. Equation for the calculation is found under method validation. Calculated values of LOD and LOQ are found in table 9. Intensities are found in the appendix in A3.

Table 9. LOD and LOQ of the method for all elements.

	Al	Ca	Fe	K	Mg	P	Na
LOD (mg/g)	0.018	0.20	0.13	0.046	0.023	0.038	0.25
LOQ (mg/g)	0.061	0.65	0.42	0.15	0.075	0.13	0.83

The determined concentrations for the blank solutions are lower than both the LOD and LOQ. Hence the determinations of their concentrations are not exact concentrations. LOD and LOQ values are much lower than the sample concentration for all elements except Na. The mean value for the Na concentration determined on the standard samples is 0.022, which is lower than both LOD and LOQ for Na. Therefore the concentration for Na is not accurately determined.

Trueness

The spiked samples are made by adding 50 % of the standard sample concentration of the metals analysed in the AL-solution according to table 10. The instrument has been controlled to be linear at 150 % of the samples concentration; therefore no problems due to non-linearity will arise. The same spiked concentration was added to both blanks and samples.

Table 10. The concentrations of the different elements added to the AL-solution.

Element	Concentration (mg/L)
Al	4.933
Ca	198.5
Fe	34.73
K	5.945
Mg	4.962
P	8.931
Na	0.699

For the blank solutions all the metals were from the spiked AL-solution. The recovery was calculated to determine an eventual bias in the method. The recovery is calculated by

subtracting the known concentration of the blanks from the measured concentration. Then dividing the determined concentrations with the concentration calculated from the stock solutions. The ratio between these concentrations is multiplied with 100 to convert the results to percentages. For the results see table 10.

Table 11. Recovery for the spiked blank solutions.

Al	Ca	Fe	K	Mg	P	Na
100%	98.4%	102.8%	104.8%	99.7%	111.9%	104%
101%	98.1%	102.6%	102.8%	98.9%	111.7%	101%
101%	97.1%	101.2%	102.9%	97.8%	111.3%	101%
101%	97.6%	101.9%	102.5%	98.9%	111.5%	98.9%
100%	96.6%	100.8%	101.3%	96.9%	110.8%	98.7%
99.5%	96.6%	100.7%	102.0%	97.4%	111.2%	101%
100%	97.3%	101.9%	102.7%	98.3%	112.1%	101%
101%	97.5%	101.2%	100.9%	97.9%	111.6%	99.6%
99.7%	96.6%	100.8%	100.6%	97.4%	110.7%	104%
102%	98.4%	102.1%	103.1%	98.6%	113.3%	111%

The mean values for the recovery are calculated from all of the single values see table 12 for the results.

Table 12. The mean recovery for each element is determined from the values in table 11.

Element	Al	Ca	Fe	K	Mg	P	Na
Mean recovery (%)	101	97.4	102	102	98.2	112	102

The mean recoveries are an indication of the bias of the method. The bias is calculated after the blank is subtracted and the concentration adjusted according to the control solution. For all elements but phosphorous the bias is less than 3 %.

14 samples were made with the same spiked AL-solution to determine the recovery for the method. The mean concentrations of the normal samples are subtracted from concentration of the spiked samples. The remaining concentrations from the spiked samples are the concentrations from the spike. The concentration determined from the spiked AL-solution is compared to the theoretical concentration of the spiked solution and the recovery is determined, see table 13.

Table 13. Recovery for the spiked samples.

Al	Ca	Fe	K	Mg	P	Na
69.3%	85.6%	63.7%	84.2%	78.6%	74.0%	60.9%
73.1%	85.8%	64.4%	85.5%	79.7%	74.8%	113%
75.7%	84.8%	66.3%	88.2%	82.2%	74.0%	119%
71.0%	82.6%	61.0%	85.9%	77.6%	70.1%	127%

78.5%	83.4%	62.1%	86.0%	78.8%	69.2%	123%
78.2%	90.0%	68.5%	88.9%	84.4%	76.2%	105%
78.4%	90.2%	66.8%	90.2%	84.5%	79.1%	116%
75.2%	84.4%	63.3%	87.2%	80.7%	73.6%	80.9%
75.2%	84.4%	63.3%	87.2%	80.7%	73.6%	80.9%
77.3%	86.5%	64.7%	89.5%	82.8%	74.5%	111%
75.8%	92.3%	67.3%	92.7%	84.9%	80.7%	72.9%
77.9%	90.0%	65.9%	91.2%	83.8%	79.9%	76.0%
93.7%	88.7%	67.4%	97.9%	86.7%	75.6%	90.9%
79.4%	90.9%	65.3%	90.5%	82.9%	76.8%	71.3%

The mean value of the recovery are calculated and found in table 14.

Table 14. Mean recovery for the elements.

Element	Al	Ca	Fe	K	Mg	P	Na
Mean recovery (%)	77.1	87.1	65.0	88.9	82.0	75.2	96.3

The acids in the AL-solution react differently in the solution with added metals already in the solution. Adding metals in the AL-solution probably changes the extraction equilibrium in the solution by lowering the extraction. The added metals in the solution push the equilibrium towards adsorption of the metals back on the soil particles; therefore the recovery is lower for the samples than for the blanks. The method is thereby sensitive to addition of metals in the solution.

One problem with not measuring the total concentrations is that there is not possible to compare the determined values with another method to control the eventual bias in the method. With this method only spiked samples and spiked blanks can be used. For the spiked samples the change in the equilibrium lowers the recovery due to the re-adsorption of the metals back to the soil particles, hence giving the method a low recovery.

Precision

The precision of the method is determined by the RSD from the results of the 14 standard samples done in the same day. The RSD is calculated by s/x*100, were s is the standard deviation and x is the mean value for the samples done on day 6. Calculated mean value, RSD and standard deviation is found in table 15.

Table 15. Table over mean values, standard deviations, and RSD for the elements measured on the standard samples.

	Al	Ca	Fe	K	Mg	P	Na
Mean value (mg/g)	0.183	7.36	1.17	0.245	0.194	0.348	0.017
Standard	0.0056	0.036	0.0080	0.0036	0.0011	0.0033	0.0010

deviation (mg/g)							
RSD (%)	3.1	0.5	0.7	1.5	0.6	0.9	6.1
RSD over several days (%)	3.0	1.4	3.4	2.4	3.0	1.7	18.0

RSD of all the elements except Al is less than 2 %. For Na the RSD is 6.1 %, which is very high. Na results are more insecure due to the determined concentration being lower than the LOD of the method. The method is not developed or optimized to measure Na concentration therefore these values are not as good as the other. The other results are good enough for the purpose of the analysis.

RSD over several days is the relative standard deviation for the first sample done for every day. The results for the RSD over several days are higher than the result for the normal RSD, see table 15. The higher RSD for the result over several days is due to day-to-day variation.

To measure sodium all glassware and plastic equipment used should be washed in acid [1] before usage to reduce contamination. It was not done the two first days, resulting in a higher insecurity and worse precision for the result of sodium on those two days.

Robustness

To determine the robustness of the method the values from the nonstandard samples are compared by t-tests to the standard samples. The different nonstandard samples are the samples done with 20 % more or 20 % less soil, and those samples where the soil is diluted in 20 % higher and 20 % lower concentrated AL-solution. The results from both these alternative methods will determine the robustness of the method. For the determination of the robustness only the samples done on the first day for the respective test was used.

Results from the samples done with 4 grams of soil are found in table 16.

Table 16. Concentration values from the samples with 4 grams of soil added instead of the standard samples with 5 gram of soil.

Sample	Al (mg/g)	Ca (mg/g)	Fe (mg/g)	K (mg/g)	Mg (mg/g)	P (mg/g)	Na (mg/g)
9 (4g) day 1	0.199	7.69	1.29	0.258	0.214	0.378	0.028
10 (4g) day 1	0.205	7.70	1.31	0.261	0.211	0.378	0.058
11 (4g) day 1	0.197	7.66	1.30	0.259	0.210	0.377	0.025
12 (4g) day 1	0.202	7.76	1.31	0.262	0.211	0.380	0.021
13 (4g) day 1	0.200	7.70	1.30	0.257	0.207	0.378	0.018
14 (4g) day 1	0.200	7.73	1.32	0.261	0.210	0.380	0.018
9 (4g) day 2	0.201	7.68	1.29	0.256	0.208	0.372	0.038

10 (4g) day 2	0.205	7.70	1.29	0.255	0.208	0.372	0.013
11 (4g) day 2	0.203	7.61	1.30	0.259	0.209	0.373	0.013
12 (4g) day 2	0.204	7.68	1.28	0.256	0.208	0.371	0.013
13 (4g) day 2	0.207	7.84	1.29	0.263	0.213	0.387	0.013
14 (4g) day 2	0.205	7.72	1.29	0.259	0.209	0.381	0.013

The values for the samples were compared to the standard samples by a two-sided t-test on excel. Results from the comparison between the standard samples and 4 grams samples are found in table 17.

Table 17. Results of the comparison between the samples done with 4 grams of soil to the standard samples. For values see table 16 and 5.

	Al	Ca	Fe	K	Mg	P	Na
Mean value (mg/g)	0.201	7.72	1.30	0.259	0.210	0.377	0.027
p-value	$4.3*10^{-6}$	$5.0*10^{-5}$	$2.1*10^{-3}$	$8.8*10^{-3}$	$2.3*10^{-5}$	$8.1*10^{-8}$	$3.0*10^{-1}$
Significant difference	Yes	Yes	Yes	Yes	Yes	Yes	No

For the calculation done in excel the difference is significant if $p < 0.05$. The calculation is used to determine whether there is a different between the two methods, the standard method and the alternative preparation method. For all elements except Na there is a difference in the final result if only 4 grams of soil is used.

One possible reason that there is no significant difference for Na is because the materials have to be prewashed with acid to remove residues, giving the results much higher standard deviation. The most significant reason that there is a difference between Na and the other elements is because the concentration of Na is lower than LOD and LOQ for the method. Concentrations below LOD are not accurately determined and the result of the Na measurement will hence not affect the total result as much as the other elements.

At the same time as the samples with 4 grams of soil, samples with 6 grams were made and in the same way an eventual difference is evaluated to determine the robustness. For the results from the 6 grams samples see table 18. For the evaluation of the results see table 19.

Table 18. Concentration for the sample made with 6 grams of soil added instead of the standard sample with 5 grams soil.

Sample	Al (mg/g)	Ca (mg/g)	Fe (mg/g)	K (mg/g)	Mg (mg/g)	P (mg/g)	Na (mg/g)
15 (6g) day 1	0.168	7.45	1.10	0.249	0.195	0.332	0.015
16 (6g) day 1	0.170	7.49	1.08	0.252	0.196	0.335	0.015
17 (6g) day 1	0.183	7.57	1.22	0.256	0.201	0.350	0.019

18 (6g) day 1	0.174	7.51	1.18	0.250	0.196	0.343	0.016
19 (6g) day 1	0.180	7.54	1.20	0.254	0.201	0.349	0.019
20 (6g) day 1	0.179	7.57	1.21	0.255	0.201	0.346	0.030
15 (6g) day 2	0.189	7.57	1.19	0.257	0.202	0.344	0.017
16 (6g) day 2	0.184	7.51	1.20	0.254	0.201	0.350	0.014
17 (6g) day 2	0.183	7.47	1.17	0.252	0.199	0.346	0.014
18 (6g) day 2	0.181	7.51	1.18	0.252	0.199	0.341	0.014
19 (6g) day 2	0.181	7.59	1.20	0.256	0.201	0.352	0.014
20 (6g) day 2	0.180	7.40	1.18	0.248	0.196	0.342	0.014

The values for the samples were compared to the standard samples by the t-test function in excel. Result from the comparison between the standard samples and 6 grams samples in table 19.

Table 19. The mean value and parameters used to determine whether the difference between the 6 grams samples and the standard samples is significant or not. For values of the different measurements see table 18 and 5.

	Al	Ca	Fe	K	Mg	P	Na
Mean value (mg/g)	0.182	7.54	1.20	0.255	0.200	0.347	0.019
p-value	0.063	0.38	$1*10^{-4}$	0.29	0.97	$1*10^{-5}$	0.95
Significant difference	No	No	Yes	No	No	Yes	No

For the calculation done in excel the difference is significant if $p < 0.05$. In the test with 4 grams of soil most of the elements gave a result that is significantly different from the standard sample. However, for the samples done with 6 grams of soil a majority of the elements gave no significant difference. Adding more soil did not affect the results as much as adding less soil.

Sample 15 and 16 was by mistake made with a different concentration on the AL-solution. The mistake with sample 15 and 16 was that instead of diluting the 100 mL AL-solution to total volume of 2 L with water, 2 L of water was added.

It seems to be a higher concentration of Al, Ca, Fe, Mg, P and Na for the samples done with 4 gram than the samples done with 6 grams of soil. The reason that the concentration for the samples done with 4 gram are higher than the samples done with 6 gram is due to the AL-solution cannot extract all metals from the samples with 6 gram soil. Therefore the concentration in mg/L is slightly higher for the samples done with 6 gram of soil; however when the amount of soil is taken account for the concentration is lower for the samples with

more soil. The results will change with different amount of soil used in the preparation. Hence it is important to use the same weight every time.

One other method in which the robustness of the method was tested was by dissolving the samples in 20 % higher and lower concentrated AL-solution. The results from the tests done with different strengths of the AL-solution will be compared to the standard samples with a t-tests on excel. For results from the samples done with 20 % higher concentrated AL-solution, see table 20.

Table 20. Concentration values for the samples done with 120% concentrated AL-solution.

Sample	Al (mg/g)	Ca (mg/g)	Fe (mg/g)	K (mg/g)	Mg (mg/g)	P (mg/g)	Na (mg/g)
1 (120%) day 3	0.196	7.80	1.28	0.252	0.194	0.380	0.019
2 (120%) day 3	0.196	7.65	1.26	0.251	0.193	0.376	0.021
3 (120%) day 3	0.198	7.67	1.29	0.253	0.196	0.381	0.019
4 (120%) day 3	0.194	7.65	1.27	0.249	0.192	0.375	0.019
5 (120%) day 3	0.197	7.71	1.29	0.251	0.196	0.382	0.019
6 (120%) day 3	0.193	7.58	1.28	0.251	0.192	0.374	0.019
19 (120 %) day 4	0.206	7.73	1.31	0.260	0.209	0.386	0.025
20 (120 %) day 4	0.204	7.67	1.31	0.256	0.205	0.382	0.025
21 (120 %) day 4	0.203	7.70	1.31	0.256	0.205	0.381	0.025
22 (120 %) day 4	0.204	7.58	1.29	0.256	0.205	0.386	0.026
23 (120 %) day 4	0.201	7.69	1.31	0.260	0.204	0.378	0.025
24 (120 %) day 4	0.204	7.71	1.31	0.261	0.208	0.379	0.027

The concentration from the measurements with 120 % concentrated AL-solution are compared to the concentrations of the standard samples with a t-test done by excel. The calculated values are compared to the critical values. There is a difference between the results if $p < 0.05$. For the mean values and evaluation of the test see table 21.

Table 21. The mean values and parameters used to determine whether the difference between the samples diluted in 120% concentrated AL-solution and the standard samples is significant or not. For values of the different measurements see table 20 and 5.

	Al	Ca	Fe	K	Mg	P	Na
Mean value	0.196	7.68	1.28	0.251	0.194	0.780	0.019

(mg/g)							
p-value	$8.1*10^{-3}$	$4.2*10^{-2}$	$5.3*10^{-13}$	$1.7*10^{-4}$	$2.3*10^{-7}$	$2.5*10^{-6}$	$3.7*10^{-4}$
Significant difference	Yes	Yes	Yes	Yes	Yes	Yes	Yes

From the results of the critical parameters in table 21, there is clear that using a higher concentrated AL-solution gives a significant different result for most elements. The determined concentrations are significant higher than for the standard samples. Hence if the Al-solution is incorrectly prepared or diluted, the results will not be correct if the concentration of the AL-solution is higher than the normal.

The final robustness test was to dilute the soil in 20 % lower concentrated AL-solution. Results from the measurements in table 22.

Table 22. Concentration values for the samples done with 80% concentrated AL-solution.

Sample	Al (mg/g)	Ca (mg/g)	Fe (mg/g)	K (mg/g)	Mg (mg/g)	P (mg/g)	Na (mg/g)
7 (80%) day 3	0.165	7.49	1.09	0.251	0.199	0.331	0.021
8 (80%) day 3	0.164	7.43	1.09	0.249	0.196	0.333	0.020
9 (80%) day 3	0.164	7.49	1.10	0.249	0.197	0.330	0.021
10 (80%) day 3	0.161	7.40	1.07	0.248	0.194	0.328	0.021
11 (80%) day 3	0.176	7.38	1.09	0.256	0.199	0.324	0.022
12 (80%) day 3	0.164	7.41	1.09	0.251	0.197	0.332	0.019
10 (80%) day 4	0.166	7.37	1.09	0.256	0.206	0.331	0.024
11 (80%) day 4	0.171	7.40	1.10	0.258	0.209	0.330	0.025
12 (80%) day 4	0.172	7.30	1.09	0.254	0.211	0.329	0.046
13 (80%) day 4	0.169	7.40	1.10	0.257	0.207	0.333	0.024
14 (80%) day 4	0.171	7.35	1.09	0.257	0.207	0.329	0.025
10 (80%) day 4	0.171	7.38	1.09	0.255	0.208	0.335	0.025

The concentrations determined are compared to the standard samples by a two-sided t-test; see table 23, to determine if there is a difference between the two preparation methods.

Table 23. Mean value and parameters used to determine whether the difference between the samples diluted in 80% concentrated AL-solution and the standard samples is significant or not. For values of the different measurements see table 22 and 5.

	Al	Ca	Fe	K	Mg	P	Na
Mean value (mg/g)	0.166	7.43	1.09	0.251	0.197	0.330	0.020

p-value	$5.3*10^{-9}$	$4.9*10^{-5}$	$1.5*10^{-8}$	$2.9*10^{-1}$	$7.7*10^{-3}$	$1.4*10^{-10}$	$6.1*10^{-1}$
Significant difference	Yes	Yes	Yes	No	Yes	Yes	No

The calculated values are compared to the critical value. If $p < 0.05$ for the calculation done by excel there is a significant difference.

With the lower concentrated AL-solution the determined concentration for the samples are lower than for the standard samples for all elements except K, and Na. The difference is that when the higher concentrated AL-solution is used the measured concentration that differed was higher than the standard samples. However for the samples done with 80 % AL-solution the concentration that differed from the standard samples was lower. These results show that the concentration of AL-solution is of great importance and that it had to be consistent for all measurements.

Day to day variation

For the day-to-day variation 8 samples per day was done for 5 days with the same method. The mean value and variance of the concentrations for each element is calculated for every day. From the calculated values the variance of the mean value and mean value of the variances are calculated, see table 24.

Table 24. Variances of mean values and mean value of the variances for each element, used to determine the day-to-day variation.

	Al	Ca	Fe	K	Mg	P	Na
MV	$8.3*10^{-6}$	$3.6*10^{-3}$	$2.8*10^{-4}$	$6.2*10^{-6}$	$3.1*10^{-6}$	$1.1*10^{-5}$	$1.5*10^{-5}$
VM	$2.5*10^{-5}$	$9.0*10^{-3}$	$1.7*10^{-3}$	$3.2*10^{-5}$	$3.2*10^{-5}$	$1.2*10^{-5}$	$2.8*10^{-5}$

The calculated value of both MV and VM is used to determine whether there is a day-to-day variation in the determined concentrations. To determine the variation F=VM*number of samples/MV is calculated, the critical value $F_{crit} = 2.64$. F-values calculated from the ANOVA are found in table 25.

Table 25. F values from the ANOVA test.

	Al	Ca	Fe	K	Mg	P	Na
F-value	24.3	20.1	46.1	42.2	81.2	26.2	15.1

For every element the F-value exceeds the critical value of 2.64. Therefore there is a clear day-to-day variation for all elements. The variance within a day is very low; however the differences between the different days are significant. The day-to-day variation is partly due to variations in the ICP-instrument.

Conclusion

The sample preparation is a simple process however the analysis is very sensitive for small changes in the method, thus it is important to be very accurate particularly when the AL-solution is prepared.

The method validation proved that the precision of the method is good since most of the elements had a low RSD. The concentration of the blank solutions and Na were lower than both LOD and LOQ and Na are hence not as accurately determined as the other elements. Conversely the method proved to be sensitive to small changes in the preparation from the robustness tests in addition to a significant day-to-day variation for all elements. The linearity was controlled partly to know that the spiked sample would not exceed the linear range of the instrument. Even though the spiked samples did not exceed the linear range the recovery for the spiked samples was around 80 % for most elements. The low recovery for the spiked samples is likely due to re-adsorption of the metals on the soil particles.

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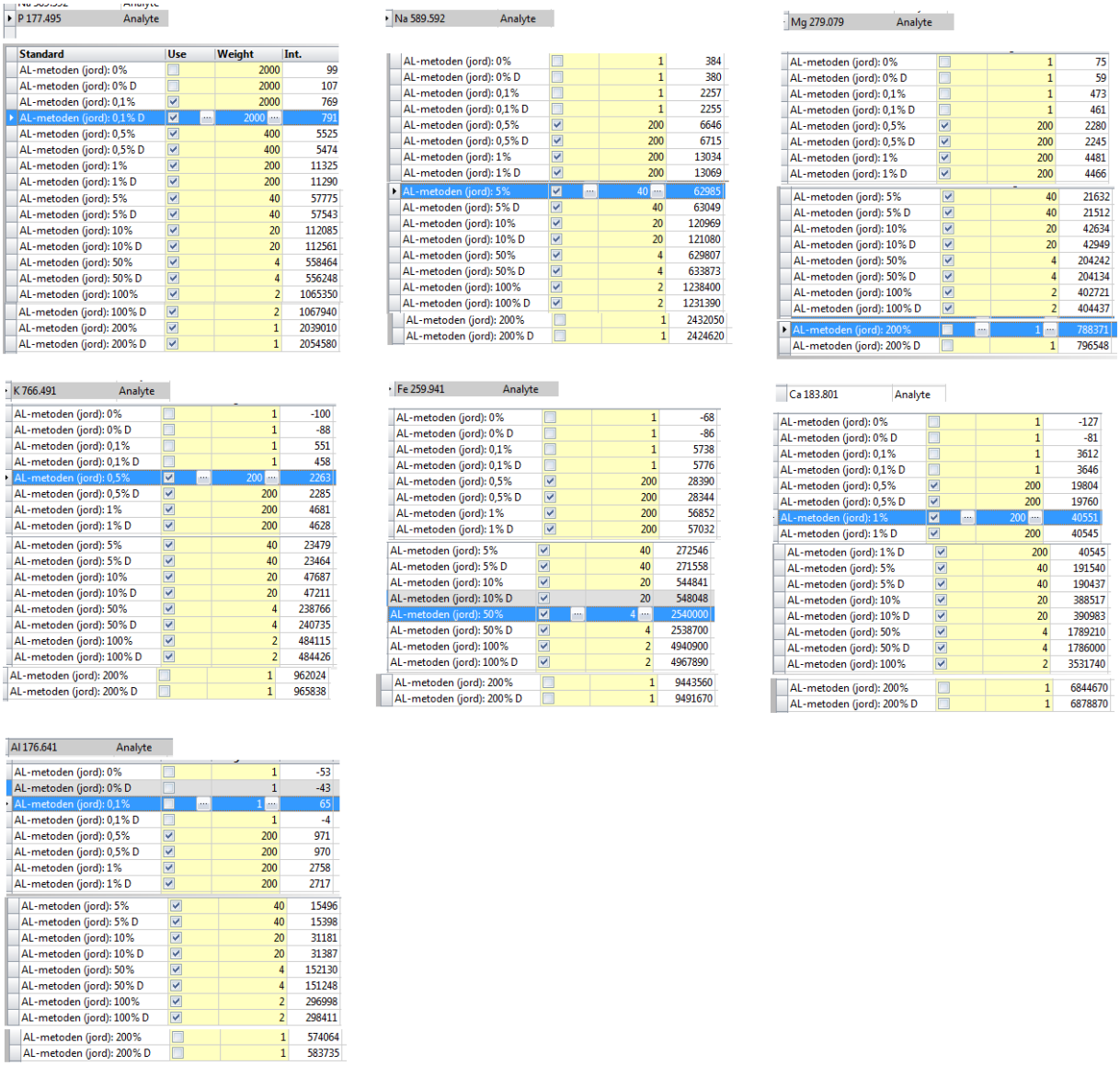
Appendix

Data from the measurments on all samples, calibration solutions and linear range solutions. The measured values for the linear range control are found in A1. The data from all measured samples and calibration, linear range and control solutions are found in A2. Intensities used for LOD and LOQ are found in A3.

A1. Shows the intensities measured for the solutions made to determine the linear range. For Ca one value for the solution with 100 % concentration was missed in the picture, the value is 3543470.



A2. All data from the samples, includes measured concentrations as well as used amount of soil and AL-solution.

Day 1			Measured concentration (mg/L)						
	Weigth (g)	Volume (mL)	Al	Ca	Fe	K	Mg	P	Na
blank	0.00	100.00	-0.02430	-0.40515	-0.07776	0.02571	-0.0607	-0.0267	0.1919
Blank	0.00	100.00	-0.02601	-0.39969	-0.00689	-0.00176	-0.0619	-0.0293	0.4913
1 (standard)	5.00	100.00	9.982	413.849	70.654	12.79	10.667	18.92	1.216
2 (standard)	5.00	100.01	9.828	410.914	68.043	12.721	10.607	18.631	1.114
3 (standard)	5.00	100.00	9.864	415.449	69.636	12.863	10.618	18.787	2.053
4 (standard)	5.00	100.00	9.801	412.544	68.165	12.776	10.581	18.638	1.301
5 (standard)	5.00	100.00	10.006	417.511	72.106	12.888	10.903	18.964	1.296
6 (standard)	5.00	100.01	9.735	408.833	69.212	12.622	10.6	18.813	1.146
7 (standard)	5.00	100.00	9.938	410.844	70.414	12.749	10.697	18.928	1.283
8 (standard)	5.00	100.00	9.959	414.081	69.576	12.905	10.709	19.094	1.527

9 (4g)	4.00	100.00	8.396	335.647	56.752	10.313	8.989	15.753	1.464
10 (4g)	4.00	100.00	8.654	336.2	57.755	10.407	8.86	15.768	2.641
11 (4g)	4.01	100.00	8.357	335.252	57.319	10.353	8.852	15.766	1.349
12 (4g)	4.00	100.00	8.526	338.49	57.921	10.474	8.856	15.86	1.173
13 (4g)	4.00	100.00	8.428	336.225	57.313	10.265	8.726	15.753	1.073
14 (4g)	4.00	100.00	8.434	337.145	58.31	10.408	8.821	15.832	1.045
15 (6g)	6.00	100.02	10.624	487.491	72.919	14.919	12.338	20.792	1.261
16 (6g)	6.00	100.00	10.762	490.555	71.63	15.094	12.414	20.975	1.25
17 (6g)	6.00	100.00	11.595	495.557	80.927	15.348	12.701	21.915	1.482
18 (6g)	6.00	100.00	11.05	491.651	78.16	15.000	12.389	21.471	1.299
19 (6g)	6.00	100.00	11.394	493.949	79.254	15.239	12.696	21.841	1.498
20 (6g)	6.00	100.00	11.348	495.444	79.999	15.285	12.738	21.684	2.163
control solution			5.318	54.578	11.034	9.889	10.553	10.437	2.983
control solution			5.266	54.657	11.045	10.057	10.621	10.454	2.992
Water			< -0.004	< -0.519	< -0.110	< -0.022	< -0.067	< -0.039	< -0.001
Day 2			Measured concentration (mg/L)						
Sample	weight (g)	Volume (mL)	Al	Ca	Fe	K	Mg	P	Na
blank	0	100.00	-0.0180	-0.42021	-0.06776	-0.03771	-0.054	-0.0331	0.1648
blank	0	100.00	-0.01799	-0.27807	0.007968	-0.0446	-0.06	-0.0295	0.3382
1 (standard)	5.00	100.00	10.186	410.719	69.113	12.758	10.782	18.667	1.28
2 (standard)	5.00	100.01	10.324	410.382	68.901	12.797	10.761	18.719	1.418
3 (standard)	5.00	100.00	10.11	412.338	67.508	12.581	10.645	18.678	1.459
4 (standard)	5.00	100.00	10.135	409.591	66.704	12.661	10.692	18.728	1.69
5 (standard)	5.00	100.00	10.07	408.501	67.442	12.378	10.513	18.563	1.674
6 (standard)	5.00	100.05	10.115	409.239	67.398	12.649	10.621	18.696	1.513
7 (standard)	5.00	100.00	9.985	405.969	66.209	12.473	10.545	18.449	1.788
8 (standard)	5.00	100.00	10.085	414.879	67.486	12.586	10.709	18.883	1.581
9 (4g)	4.00	100.01	8.478	331.613	55.797	10.008	8.655	15.411	1.759
10 (4g)	4.00	100.00	8.644	332.648	55.889	9.987	8.663	15.428	0.7561
11 (4g)	4.00	100.00	8.534	328.839	56.236	10.119	8.691	15.471	0.7587
12 (4g)	4.00	100.00	8.587	331.838	55.208	10.027	8.64	15.352	0.7809
13 (4g)	4.00	100.00	8.732	338.532	55.79	10.297	8.865	16.028	0.7831
14 (4g)	4.00	100.00	8.618	333.345	55.803	10.128	8.711	15.77	0.767
15 (6g)	6.00	100.01	11.962	490.398	77.24	15.111	12.639	21.405	1.254
16 (6g)	6.00	100.00	11.627	486.611	77.427	14.956	12.571	21.763	1.081
17 (6g)	6.00	100.00	11.538	484.339	76.096	14.807	12.424	21.51	1.07
18 (6g)	6.00	100.00	11.459	486.937	76.473	14.8	12.443	21.2	1.066
19 (6g)	6.00	100.01	11.454	491.828	78.008	15.068	12.586	21.878	1.095
20 (6g)	6.00	100.00	11.361	479.500	76.371	14.576	12.235	21.237	1.095
control solution			5.294	54.037	10.836	9.864	10.514	10.355	2.964
water			< 0.0160	< 0.0113	< 0.0014	< 0.0351	< 0.0539	< 0.0008	< 0.0050
Control solution			5.254	54.09	10.769	9.78	10.413	10.404	2.95
Day 3			Measured concentration (mg/L)						
Sample	Weight (g)	Volume (mL)	Al	Ca	Fe	K	Mg	P	Na
blank	0	100.00	-0.02664	-0.31602	-0.08256	-0.04075	-0.0532	-0.0281	0.0366

blank	0	100.00	-0.02044	-0.26686	-0.09361	-0.03538	-0.0693	-0.0276	0.0353
1 (120%)	5.01	100.02	10.264	424.555	69.955	12.469	10.13	19.78	0.9585
2 (120%)	5.00	100.02	10.272	415.879	68.805	12.417	10.051	19.529	1.091
3 (120%)	5.01	100.00	10.385	417.895	70.686	12.523	10.246	19.849	0.9911
4 (120%)	5.02	100.01	10.212	417.512	69.605	12.368	10.075	19.557	0.9861
5 (120%)	5.02	100.00	10.349	420.857	70.53	12.477	10.257	19.947	0.9621
6 (120%)	5.02	100.00	10.139	413.674	69.847	12.447	10.041	19.552	0.9859
7 (80%)	5.02	100.00	8.65	408.898	59.354	12.451	10.408	17.301	1.065
8 (80%)	5.01	100.00	8.614	404.918	59.229	12.354	10.258	17.365	1.031
9 (80%)	5.01	100.00	8.61	407.804	59.897	12.36	10.314	17.206	1.063
10 (80%)	5.03	100.00	8.482	404.867	58.538	12.362	10.185	17.179	1.068
11 (80%)	5.01	100.00	9.21	401.891	59.507	12.674	10.38	16.896	1.125
12 (80%)	5.02	100.01	8.6	404.23	59.516	12.464	10.299	17.323	0.9691
13 (standard)	5.01	100.00	9.555	412.225	68.797	12.532	10.317	18.276	1.083
14 (standard)	5.02	100.00	9.56	409.398	69.56	12.447	10.502	18.492	1.185
15 (standard)	5.00	100.04	9.342	411.195	69.058	12.355	10.29	18.605	0.9488
16 (standard)	5.02	100.00	9.48	412.525	70.5	12.584	10.333	18.316	0.9357
17 (standard)	5.00	100.00	9.327	414.994	68.49	12.426	10.345	18.531	0.9077
18 (standard)	5.03	100.01	9.525	405.22	69.224	12.513	10.314	18.447	0.9442
19 (standard)	5.00	100.01	9.351	410.253	69.128	12.341	10.247	18.589	0.9303
20 (standard)	5.00	100.00	9.33	410.447	69.577	12.295	10.271	18.471	0.9465
Blank unfiltered			-0.02224	-0.46241	-0.08573	-0.04161	-0.0783	-0.0296	0.0224
Blank unfiltered			-0.0244	-0.4496	-0.02091	-0.01895	-0.0627	-0.0241	0.0279
Water			-0.00635	-0.51314	-0.10923	-0.03332	-0.0694	-0.0359	-0.0054
control solution (10%)			5.26	54.417	10.874	9.831	10.495	10.458	2.988
control solution (10%)			5.24	54.384	10.954	10.01	10.493	10.373	2.984
Day 4			Measured concentration (mg/L)						
Sample	Weight (g)	Volume (mL)	Al	Ca	Fe	K	Mg	P	Na
blank	0	100.00	-0.01821	-0.2462	-0.07398	-0.03759	-0.0359	-0.0251	0.3619
blank	0	100.00	-0.02277	-0.3857	-0.09216	-0.05331	-0.0438	-0.0331	0.1921
1 (standard)	5.00	100.01	9.691	407.029	66.959	12.204	10.54	18.26	0.9399
2 (standard)	5.00	100.00	9.877	415.228	68.28	12.332	10.675	18.898	0.9136
3 (standard)	5.01	100.00	9.73	407.207	66.847	12.302	10.56	18.316	1.234
4 (standard)	5.00	100.00	9.876	417.989	68.446	12.283	10.537	18.101	1.406
5 (standard)	5.00	100.18	9.642	404.045	66.334	12.106	10.442	18.247	1.239
6 (standard)	5.00	100.00	9.9	413.769	67.29	12.5	10.776	18.563	1.384
7 (standard)	5.02	100.00	9.454	413.722	65.578	12.083	10.415	18.074	0.8954
8 (standard)	5.01	100.01	9.797	412.664	67.413	12.509	10.637	18.652	0.9358
9 (80%)	5.01	100.00	8.713	401.984	59.254	12.273	10.524	17.005	0.8897

10 (80%)	5.01	100.02	8.978	403.35	59.772	12.368	10.699	16.929	0.9217
11 (80%)	5.01	100.01	9.053	397.855	59.354	12.178	10.771	16.869	1.973
12 (80%)	5.00	100.00	8.849	402.869	59.33	12.268	10.566	17.05	0.8856
13 (80%)	5.00	100.00	8.95	400.098	59.187	12.287	10.561	16.838	0.9108
14 (80%)	5.00	100.02	8.959	401.299	59.094	12.17	10.599	17.145	0.9045
15(120%)	5.00	100.00	10.804	420.756	71.21	12.446	10.673	19.806	0.9141
15(120%)	5.00	100.00	10.67	417.264	71.011	12.21	10.455	19.628	0.9012
15(120%)	5.00	100.00	10.646	418.981	70.967	12.243	10.449	19.56	0.9105
15(120%)	5.02	100.00	10.709	414.326	70.204	12.265	10.497	19.882	0.979
15(120%)	5.00	100.02	10.552	418.55	70.846	12.417	10.406	19.407	0.9331
15(120%)	5.00	100.00	10.69	419.337	71.036	12.466	10.629	19.448	1.028
control solution (10%)			5.232	54.574	10.992	9.746	10.508	10.451	2.951
Water			-0.00439	-0.52048	-0.10895	-0.02235	-0.0562	-0.0359	-0.0001
blank unfiltered			-0.02512	-0.46448	-0.08502	-0.04795	-0.0546	-0.0333	0.0212
blank unfiltered			-0.01830	-0.44989	-0.02018	-0.05557	-0.0609	-0.0275	0.0217
control solution (10%)			5.268	54.356	10.95	9.854	10.512	10.413	2.948

Day 5			Measured concentration (mg/L)						
Sample	Weight (g)	Volume (mL)	Al	Ca	Fe	K	Mg	P	Na
Control solution 10%			5.22	53.551	10.805	9.804	10.399	10.237	2.985
Spiked blank	0.00	100.00	5.14	207.306	38.134	6.04	5.049	10.185	0.7941
Spiked blank	0.00	100.00	5.168	206.743	38.066	5.925	5.004	10.172	0.7705
Spiked blank	0.00	100.00	5.124	204.632	37.546	5.927	4.95	10.132	0.7731
Spiked blank	0.00	100.00	5.16	205.613	37.805	5.907	5.006	10.147	0.7585
Spiked blank	0.00	100.00	5.107	203.661	37.39	5.838	4.906	10.084	0.7568
Spiked blank	0.00	100.00	5.073	203.637	37.365	5.879	4.931	10.124	0.77
Spiked blank	0.00	100.00	5.119	205.106	37.783	5.916	4.976	10.208	0.7748
Spiked blank	0.00	100.00	5.163	205.408	37.55	5.816	4.956	10.158	0.7631
Spiked blank	0.00	100.00	5.084	203.54	37.381	5.796	4.928	10.078	0.7941
Spiked blank	0.00	100.00	5.187	207.331	37.864	5.965	4.99	10.32	0.8414
Spiked sample 1	5.00	100.03	13.139	582.416	89.517	17.378	14.376	25.148	1.58
Spiked sample 2	5.00	100.00	13.327	582.733	89.773	17.453	14.426	25.226	1.946
Spiked sample 3	5.00	100.00	13.455	580.828	90.431	17.616	14.553	25.153	1.988
Spiked sample 4	5.00	100.00	13.225	576.464	88.577	17.479	14.325	24.798	2.04
Spiked sample 5	5.02	100.07	13.594	577.989	88.985	17.484	14.386	24.724	2.014
Spiked sample 6	5.00	100.00	13.58	591.226	91.192	17.656	14.664	25.349	1.891
Spiked sample 7	5.00	100.00	13.59	591.482	90.604	17.737	14.667	25.608	1.963
Spiked sample 8	5.00	100.01	13.432	580.056	89.373	17.558	14.477	25.113	1.72

Spiked sample 9	5.02	100.95	13.432	580.056	89.373	17.558	14.477	25.113	1.72
Spiked sample 10	5.00	100.00	13.537	584.315	89.884	17.694	14.581	25.194	1.928
Spiked sample 11	5.00	100.00	13.46	595.675	90.781	17.882	14.687	25.75	1.664
Spiked sample 12	5.01	100.00	13.563	591.123	90.296	17.797	14.63	25.677	1.686
Spiked sample 13	5.00	100.00	14.345	588.535	90.817	18.19	14.775	25.297	1.79
Spiked sample 14	5.00	100.00	13.638	593.053	90.097	17.755	14.586	25.398	1.653
control solution			5.158	52.786	10.587	9.663	10.182	10.205	2.912
Water			< -0.007	< -0.518	< -0.111	< -0.029	< -0.050	< -0.039	< 0.0011

Day 6			Measured concentration (mg/L)						
Prov	Weight (g)	Volume (mL)	Al	Ca	Fe	K	Mg	P	Na
blank	0	100.00	-0.01346	-0.20113	0.018485	-0.0075	-0.0358	-0.0004	0.2586
blank	0	100.00	-0.02718	-0.31342	-0.07282	-0.02698	-0.0472	-0.0312	0.0579
blank	0	100.00	-0.01926	-0.26004	-0.08153	-0.02711	-0.0478	-0.031	0.0481
blank	0	100.00	-0.01919	-0.37667	-0.09082	-0.01598	-0.0476	-0.0325	0.0449
blank	0	100.00	-0.02011	-0.31777	-0.0939	-0.02997	-0.0395	-0.0345	0.0387
blank	0	100.00	-0.02507	-0.37461	-0.09193	-0.0492	-0.0395	-0.0268	0.0323
1 (standard)	5.00	100.00	9.32	397.048	63.839	11.865	10.014	18.006	0.8803
2 (standard)	5.01	100.00	9.355	399.103	63.445	11.816	10.034	17.973	0.893
3 (standard)	5.00	100.00	9.31	400.482	63.629	11.779	9.997	18.033	0.8809
4 (standard)	5.00	100.31	9.323	392.577	62.662	11.789	9.969	17.731	0.8989
5 (standard)	5.00	100.00	10.024	399.259	63.608	12.125	10.142	17.95	0.991
6 (standard)	5.01	100.00	9.389	397.607	62.843	11.922	10.016	17.81	0.8733
7 (standard)	5.00	100.01	9.277	395.793	62.517	11.78	9.974	17.886	0.871
8 (standard)	5.00	100.00	9.433	395.968	63.142	11.807	10.042	17.84	0.903
9 (standard)	5.01	100.00	9.49	397.608	63.491	11.858	10.091	18.12	0.8933
10 (standard)	5.00	100.02	10.26	396.229	63.808	12.37	10.119	17.872	1.042
11 (standard)	5.00	100.00	9.696	397.398	62.957	12.139	10.106	18.241	0.9726
12 (standard)	5.00	100.00	9.47	400.731	63.199	11.881	10.039	18.069	0.9277
13 (standard)	5.01	100.00	9.442	398.784	62.946	11.85	10.051	17.947	0.9335
14 (standard)	5.00	100.00	9.674	399.68	63.739	11.979	10.129	18.374	0.9557
control solution			5.24	53.924	10.847	9.714	10.401	10.341	2.968
Water			< -0.002	< -0.524	< -0.108	< -0.023	< -0.063	< -0.039	< -0.004
Control solution			5.176	54.136	10.817	9.755	10.438	10.379	2.967

A3 Intensity for the single measurements on the blanks used for LOD and LOQ calculations.

Al	Ca	Fe	K	Mg	P	Na
-111.046	2126.98	5578.18	38.986	150.425	510.27	10820.4
-54.14	2112.14	7008.38	93.838	186.498	546.31	10743
-202.175	1369.55	1693.46	-32.818	110.1	173.99	2780.04
-129.595	1317.69	1739.94	-18.737	134.716	215.9	2718.67
-106.86	1692.51	1265.3	-35.742	161.439	213.1	2390.72
-128.723	1732.47	1294.88	-17.05	79.197	180.78	2325.04
-117.159	882.837	781.709	39.774	122.398	175.61	2206.26
-117.601	930.189	846.546	12.753	119.307	187.01	2247.19
-100.616	1334.78	661.759	-37.267	132.493	149.42	1958.06
-145.269	1292.36	657.816	-42.626	174.83	169.93	2000.29
-135.264	977.29	741.358	-57.524	164.439	198.65	1767.62
-170.801	864.213	776.518	-204.394	143.215	287.03	1680.84