Geochemistry laboratory: method description

Till Geochemistry by Nitric Acid (HNO_3) partial leaching at the Geological Survey of Sweden

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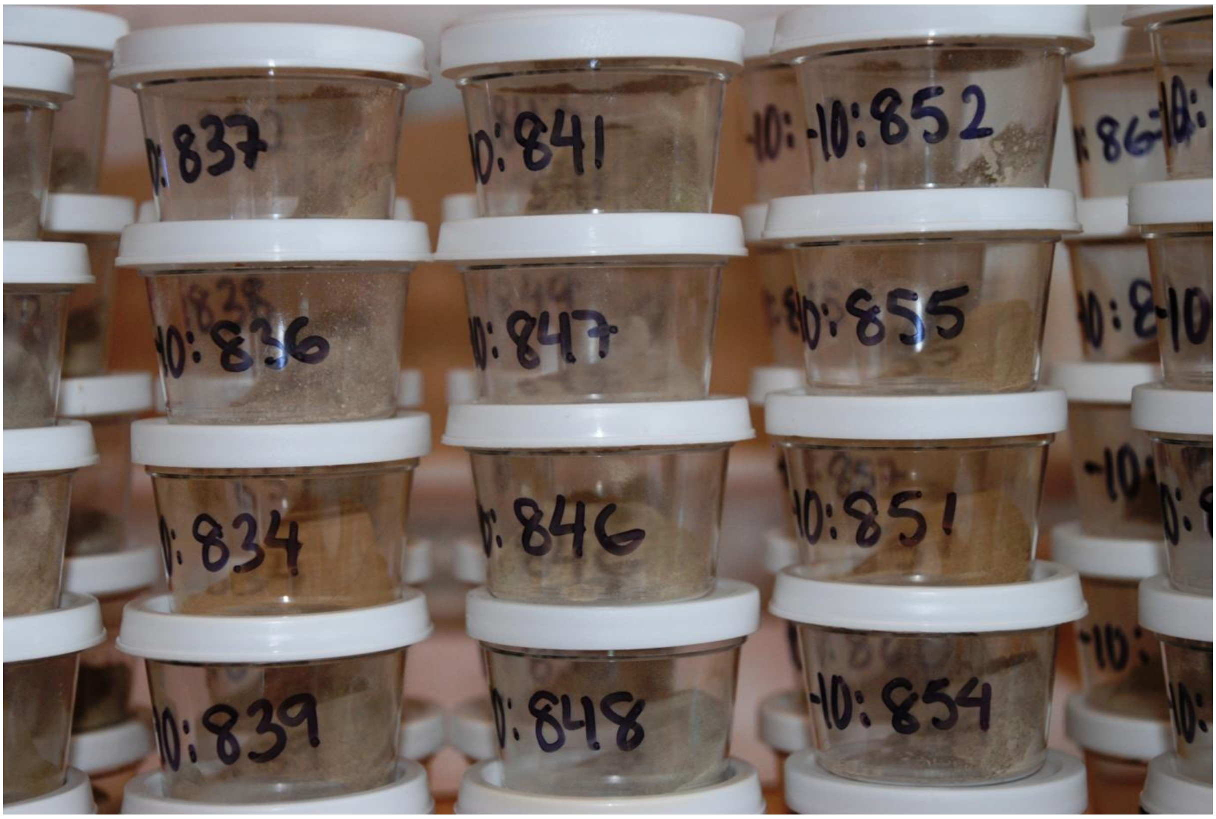

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Corrections made 12 January 2018:
Table 1 and Table 2 added, pages 10 and 11.

Corrections made 14 September 2020:
Table 1, page 10
Incorrectly calculated values for extractability have been replaced with correct ones.

Cover photograph: Till samples, vacuum dried,
sieved to <63µm and ready for analysis.
Photographer: George Morris

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SUMMARY

As part of its routine soil geochemistry mapping program, the Geological Survey of Sweden, SGU, has developed a method for partial-leach extraction in nitric acid for subsequent analysis by inductively coupled plasma mass spectrometry (ICP-MS) The method is adapted from a Swedish Standard technique in order to account for the large volume of samples required for a regional mapping program as well as for the use of modern equipment. This report provides a sufficiently detailed description of the method so that users can produce data that is directly comparable to data found in the national database and available from SGU for their own projects. The report includes information regarding percentage extractability, precision and accuracy, and serves as the reference for SGUs method.

The report will be available in Swedish during 2018.

SAMMANFATTNING

Som en del av rutininerna för den markgeokemiska kartläggningen har Sveriges geologiska undersökning, SGU, utvecklat en metod för partiell upplösning med användning av salpetersyra för analys av induktivt kopplad plasma masspektrometri. Metoden är baserad på svensk standardteknik för att vara anpassad till den stora mängd prover som krävs i ett regionalt kartläggningsprogram samt för användning av modern utrustning. Denna rapport beskriver metoden tillräckligt detaljerat för att användarna ska kunna producera data som är direkt jämförbara med data i SGUs nationella databas. Rapporten utgör också SGUs referens för denna metod och innehåller för syftet relevant information så som procentuell extraherbarhet, precision och noggrannhet statistik.

Denna rapport kommer publiceras på svenska under 2018.

INTRODUCTION

As part of its routine soil geochemical mapping program, the Geological Survey of Sweden (SGU) carries out metal concentration determinations in till and other sediment samples using a 7molar nitric acid (7N HNO_3) partial leach, which is subsequently analysed by inductively coupled plasma - mass spectrometer (ICP-MS). The partial leach technique preferentially attacks the more soluble minerals and absorbed metal ions. This enhances their concentration in the resultant solution when compared to that of total concentration analysis.

Comparison between partial leach results and those of the total concentration method provide important information about an elements extractability in a given sample media. This knowledge can be used in risk assessments in areas with high metal concentrations (natural and anthropogenic) where serious concern regarding the groundwater and soil quality exists.

SGUs method for partial leaching by 7N HNO_3 is based upon the Swedish Standard method SS 02 83 11 (Swedish Standards Institute, 1997). This method has been adapted for use with large sample numbers and updated for use with modern equipment (ICP-MS). The principle modification compared to the Swedish Standard method is the use of open-container digestion on a hotplate or in a heating block, in place of autoclave digestion. This modification has a two-fold advantage; first, the use of a larger sample sizes permits a reduction in minimum detection limits and; second, time-efficiency is increased, a significant advantage with respect to the large number of samples required by SGU’s geochemical mapping campaigns. To date, over 29,000 samples have been analysed at SGU using this method and provide a uniform and level database covering ca 40 % of the country. The geochemical mapping is an ongoing programme with the aim of completing full Swedish coverage at a sample density of 1 sample per ca 2.5 km^2.

This report provides a detailed description of the partial leach technique in use at SGU. It is designed to provide a method description which can be used by other laboratories in order to produce results comparable to data found in the national database provided by SGU. It is also designed to provide a method reference for those using SGU data.

EQUIPMENT

ICP-MS	**1995–2007**	**Perkin Elmer Elan 5000 A**
	2007–	Perkin Elmer Elan 9000
Hotplate	1995–2013	Ceran 500
	2013–	Perkin Elmer SPB 50-72
Sample digestion vessels	1995–2013	250ml Pyrex beakers, reusable
	2014–	50ml polypropylene sample tubes, disposable
40ml centrifuge tubes		disposable

REAGENTS

HNO_3	J.T. Baker reagent grade 70% Nitric Acid
Ultrapure Water	Filtered and deionised water from a Milli-Q Academic system

INTERNAL AND INTERNATIONAL STANDARDS

MP2 and MP3 are SGUs in-house till standards and are analysed as both a known standard at the beginning and end of each analytical run, and as a hidden unknown approximately every 20th sample. MP2 supersedes SGUs former in-house standard MP1 and was collected from the same locality in Norrbotten County, northern Sweden. In 2015 we began to introduce MP3, a third in-house standard collected from the same site, which will supersede MP2 when that standard runs out.

Standard Name	MP2, MP3
Location (RT 90)	1729995 7512803
Collected by	MP2: Kaj Lax, July 2006 MP3: George Morris, August 2015
Sample description:	Homogeneous till sample collected from the C-horizon between 0.7 and 1m depth. Vacuum-dried and sieved to <0.63µm

The SGU laboratory routinely runs the following internationally certified standards: **RTC-CRM022**, **RTC-CRM028** and **RTC-CRM048**. These commercial certified reference materials are Loam (CRM022), Sandy Loam (CRM028) and Clay (CRM046).

CALIBRATION SOLUTIONS

The following two in-house calibration solutions, mixed from standard solutions of known element concentrations, are used for the major element series:

H1 contains: 250 ppb Al, Ca and Fe; 100 ppb Mg; 50 ppb K; 25 ppb Na, P, Ti, Mn, Ba; 20 ppb Ce; and 10 ppb V, Cr, Rb, Sr, Y, La, U.
H2 contains: 500 ppb Al, Ca and Fe; 200 ppb Mg; 100 ppb K; 50 ppb Na, P, Ti, Mn, Ba; 10 ppb Ce; and 5 ppb V, Cr, Rb, Sr, Y, La, U.

The following two in-house calibration solutions are used for the trace element series:

S1: 5 ppb of Ni, Cu, Zn, Ba and 10 ppb of Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Th, Tm, Yb, Y, B, Ge, Mo, Nb, P, Re, Si, S, Ta, Ti, W, Zr, Li, Be, Co, As, Se, Ag, Cd, Sn, Tl, Pb, Bi, U, Sb
S2: 10 ppb of Ni, Cu, Zn, Ba and 20 ppb of Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Th, Tm, Yb, Y, B, Ge, Mo, Nb, P, Re, Si, S, Ta, Ti, W, Zr, Li, Be, Co, As, Se, Ag, Cd, Sn, Tl, Pb, Bi, U, Sb

A 5 ppb spike of In is also run as an internal standard with every sample and standard.

PROCEDURE

Sampling and Sample Preparation

The sampling and sample preparation of till is common to all analytical methods carried out at SGU or contracted in from external laboratories. Samples are collected and prepared in bulk, then split for individual analytical methods.

Till samples should meet the following criteria: they must be representative of the locality and, preferably, belong to the sand or sandy-silt size fraction. Further, potentially contaminated sites should be avoided unless this is the specific target of the project.

The distance between sample sites is ca 2.5 km, giving a ca 15 samples per 100 km^2. Sampling is carried out from a pit dug through the soil profile using a shovel and spike. Approximately 0.5 kg of sample is collected from the C horizon (typically between 0.7 to 1.2 meters depth) at the pit bottom.

Till samples are vacuum-dried and sieved with a 0.063 mm mesh nylon sieve. This reduces the sample, prior to analysis, to the so-called fine fraction (<0.063 mm) which almost exclusively contains mono-mineral grains. Coarser fractions consist of multi-mineral grains which increase the level of variation seen in repeat sampling and analysis. It is therefore much more difficult to take comparable samples while maintaining reproducibility in analyses for the coarser fractions. The fine fraction need not be milled prior to analysis, which could otherwise increase the risk of unwanted contamination of the samples.

Hidden standard and Randomisation

Quality control and quality assurance for both in-house methods and for bought in data at SGU follows a two-fold approach (after Lax & Selinus 2005). The first approach uses hidden in-house standards (MP2 or MP3) that are inserted into the analytical series every 10–20 samples after randomisation and run as unknowns. This reveals any systematic errors during an analytical run. Field repeats are used as a second quality assurance measure. These are collected from the same hole at the same time as, and blended with the corresponding regular sample, split on site before being given their own unique sample number. From this point until the final quality control, the repeat samples are treated as regular unknown samples. Hidden standard and repeat samples account for approximately 10% of samples overall.

Randomisation of samples is used to spread any systematic variation or error from the analytical instrument or lab over the whole data series. By analysing samples in a random order rather than based upon the order of collection, which is often related to geographical location, any error is spread over the entire study area rather than introducing false boundaries or gradients into the final data set.

The locations of hidden standards as well as the randomisation and field duplicate keys are not seen by the analytical lab thereby providing a form of independent verification of results. Data gathered from these repeat analyses of the same standard allows the precision of the method to be calculated and ensures a level dataset, i.e. comparable data of similar values and quality for given elemental concentrations in soil, over the longer term.

Acid Leaching

7N HNO_3 is mixed from 1 part ultrapure water and 1.4 parts concentrated HNO_3 (70%, 16 M) by weight.

2g of dried and sieved unknown sample (<63µm) or standard (MP2, MP3 or CRM) is weighed into a new polypropylene 50ml sample vessel.

The heating block is pre-heated to 115°C.

10ml of 7N HNO_3 is added to each sample which is gently shaken to ensure complete mixing of acid and powder. If samples are suspected to be carbonate rich, this process must be carried out slowly to prevent the reaction overflowing the sample vessel. Samples are then heated in the heating block for 47 minutes before being removed and allowed to cool.

Samples are made up to 25ml using ultrapure water and allowed to settle overnight. The following day, the resultant supernatant liquid is decanted into new 40ml centrifuge tubes.

Method blanks are prepared in the same way but exclude sample or standard.

Note: prior to 2013 reusable Pyrex beakers were the standard sample vessels. After 2013 one-time use polypropylene tubes became standard. Prior to this change, samples were heated at a higher temperature (approx. 180°C) for 30 minutes. The new longer heating time was established empirically to produce the same degree of leaching and therefore the same percentage of extractability at the lower temperature required for the use of polypropylene sample vessels.

Analytical Procedure (Analytical Conditions)

Samples are run in two series. After allowing the remaining sediment to settle, two aliquots are removed from the supernate fluid of each sample and standard. The first aliquot is diluted x500 and the second is diluted x7500. This optimises the concentration ranges for ICP-MS analysis. These are known as the Spår (trace element) and Huvud (major element) Element Series respectively. A 5ppb Indium spike is added to each blank, standard or unknown for correction of machine variation. Elements analysed with each aliquot are listed in Table 1 along with estimated extractability percentages based on a range of reference and sample materials. Barium (Ba) and Uranium (U) are run at both the x500 and x7500 dilution levels as an internal control.

At the beginning of each series a method blank is run to establish background levels. This is followed by the appropriate calibration solutions (see above) for the series, either S1 and S2 for the low dilution (spar element/trace element) series, or H1 and H2 for the high dilution (huvud element/major element) series. Solutions derived from each of the certified reference materials (RTC-CRM022, RTC-CRM028, RTC-CRM048), and from the in-house standard (MP2 or MP3) are then run. The main analytical series of unknowns and hidden standards is then run. This series includes an in-house standard (MP2 or MP) analysed as a known/open standard every 40 samples in order to monitor instrument performance. Each analytical series is terminated with an in-house standard analysed as an open/known standard.

Quality Control

The challenge of quality control with this partial leach technique is two-fold. In the first place, as a partial-leach technique, certified values for international standards cannot be used directly as the values obtained do not represent the total concentration of the element in the standard (see Table 1). The aim of quality control is to obtain consistent data for all standards, both internal and international to show that the same degree of partial leaching (consistent extractability) is obtained every time. The second challenge of quality control is that, having been developed to address the needs of large scale regional till surveys, SGUs method is currently unique. This means that direct comparative trials with outside laboratories cannot be used to test the analytical quality of the obtained results. The aim of quality control is therefore to achieve an internal constancy within the dataset.

SGUs routine quality control relies on 4 tests: regular analyses of SGUs in-house standard MP2 hidden within the unknown sample series; regular analyses of international standards at the beginning and the end of every analytical series; hidden repeat samples taken in the field at the same time as the original sample and run entirely separately throughout the system (duplicate sample); and routine comparison with external labs running similar methods.

MP2/MP3, SGUs in-house till standard, is run every 20 samples as an unknown. Mean, median, standard deviation and the coefficient of variation (%CV) are monitored for outliers and time-resolved drift of the instrument. As a first monitor of quality, the %CV on MP2/MP3 results is calculated with results <10% being considered acceptable. Where problems are suspected, control diagrams showing both unknown samples and the internal standard are used to rapidly visualise any deviation in concentrations. Based on the standard deviation in MP2/MP3 results, two levels are established: 1, MP2/MP3 standards lying outside +/- 2σ are considered cause for concern and those, plus unknown data run around the same time are examined in more detail, re-runs may be ordered; and 2, +/- 3σ on MP2/MP3 concentrations is considered the fail criteria and standards lying outside these levels are automatically re-run with the related unknown samples. Common cause for failure is instrument problems or a failure in lab routine. Element concentrations for MP2/MP3 are also monitored over the longer term to ensure consistency between analytical series. This data is monitored in a similar fashion to MP2/MP3 data within each series.

International Standards RTC-CRM022, RTC-CRM028 and RTC-CRM048are run in addition to the MP2/MP3 standards at the beginning of each analytical series and collected over time. This data is monitored in a similar fashion to the MP2/MP3 data within each series and expected concentrations for partially leached standards along with levels for concern and failure for each element in each standard are defined.

Duplicate analysis are collected in the field. Approximately every 20 samples, a second sample is taken from the same site, blended with the first then split into two sample bags and given a separate number. From this point onwards, the two samples are treated entirely separately. Comparison of the results provides an additional control on sample handling and lab procedures.

External verification of results, SGU routinely (once or twice a year) re-analyses samples at external laboratories that run partial or total extraction techniques. Due to the (currently) unique nature of SGUs method, identical results from external labs are not expected, however, a consistent difference between SGU and data by another method is expected. In addition, SGU routinely takes part in an international laboratory proficiency program, GeoPT testing run by the International Association of Geoanalysts (e.g. Thompson et al., 1996).

Limit of Detection, Limit of Quantification and Precision

Limit of Detection (LOD) is calculated based on three times the standard deviation of multiple method blanks (after JCGM, 2008). Blanks are 10ml aliquots of 7N HNO3 prepared as for regular samples (above) which are then heated and diluted exactly as regular samples. Due to the low concentrations of elements, the standard deviation is calculated based on raw counts per second (cps) and the cps of elements from a well known standard is used as a multiplier to obtain the ppm data presented in Tables 1 (major elements) and 2 (trace elements). LOD values are presented for the three major time periods over which the SGU lab has run this method and a two orders of magnitude improvement can be seen reflecting significant improvements in the instrumentation and method. When using SGU data analysed with this method, it is important to observe the correct LOD for the time period in which the data was analysed.

Limit of Quantification (LOQ) is determined in the same way as the LOD values presented above, but is quoted as ten times the standard deviation of multiple method blanks (after JCGM, 2008; Table 1: major elements; Table 2: trace elements).

Precision is derived from the multiple analyses of the hidden standard MP2. This is based on the Coefficient of Variation (%CV: 100 x (standard deviation/concentration)). Unlike the LOD, this coefficient shows little variation over time, which probably reflects variation in this natural standard rather than the improvements in instrumentation and method detailed above. (Table 1: major elements; Table 2: trace elements).

Table 1. Major element (*huvudelement*) method Limits of detection and quantification, Total concentration and extractability for MP2, as well as expected partial leach extraction values for MP2 and MP3 by this method. All values in parts per million (ppm) or percent (%) as appropriate. Current values are given in large italic numbers.

	1995–2007	**2007–2013**	**2013–present**		**MP2**	**MP2**	**MP3**	**Extract-ability**	**1995–2007**	**2007–2013**	**2013– present**	
	Limit of detection[1]	*Limit of detection*[1]	*Limit of detection*[1]	*Limit of quantification*[1]	*Total concentrations by XRF or ICP-MS*[2]	*Expected values*[3]	*Expected values*[4]	*%*[5]	*%CV*	*%CV*	*%CV*	*+/- ppm for concentration of MP2*
Na		100	2	7	28270	199	210	0,7		26	16	29
Mg	302	51	2	8	15195	5777	6586	38,0	9	10	8	425
Al	265	38	5	16	75100	13448	15345	17,9	7	11	9	1205
P	44		18	60	1260	1143	1303	90,7	5	11	8	93
K	166	604	45	150	20660	2256	2809	10,9	8	12	9	197
Ca	715	422	38	128	25300	2932	4055	11,6	7	42	8	269
Ti	30	7	1	4	6235	1162	1356	18,6	8	12	10	110
V	5	1,2	0,10	0,35	127,44	37	41	28,8	13	10	7	3
Cr	1	4,8	0,32	1,06	81,85	27	30	33,1	12	10	8	2
Mn	39	2,1	0,22	0,74	700	203	216	29,1	7	10	7	14
Fe	1398	165	11	37	55645	16832	20360	30,2	7	10	7	1205
Rb	2	0,6	0,02	0,07	70,92	22	25	30,9	13	8	6	1
Sr	5	2,7	0,04	0,14	288,71	14	16	4,9	14	12	9	1
Y	2	0,3	0,01	0,04	37,00	8	9	22,9	12	10	8	1
Ba	4	0,98	0,14	0,46	683,13	80	94	11,7	12	7	6	5
La	2	0,2	0,02	0,06	46,59	21	23	46,1	11	10	7	1
Ce		2	0,03	0,09	112,07	60	60	53,2		9	7	4
U	0,1	0,1	0,02	0,07	2,99	1,2	1,4	41,4	11	8	8	0,1

[1] Based on the standard deviation of method blank analyses
[2] Analysed at the WSU Geoanalytical labs, see Johnson et al. (1997) for method description
[3] Based on the average of 228 analyse
[4] Based on the average of 6 analyse
[5] From the ratio of partial leach to total concentration data using the MP2 standard

Table 2. Trace element (*spårelement*) method Limits of detection and quantification, Total concentration and extractability for MP2, as well as expected partial leach extraction values for MP2 and MP3 by this method. All values in parts per million (ppm) or percent (%) as appropriate. Current values are given in large italic numbers.

	1995–2007	**2007–2013**	**2013–present**		**MP2**	**MP2**	**MP3**	**Extractability**	**1995–2007**	**2007–2013**	**2013–present**	
	Limit of detection[1]	*Limit of detection*[1]	*Limit of detection*[1]	*Limit of quantification*[1]	*Total concentrations by XRF or ICP-MS*[2]	*Expected values*[3]	*Expected values*[4]	*%*[5]	*%CV*	*%CV*	*%CV*	*+/- ppm for concentration of MP2*
Li	1		0,005	0,017		10,8	15,26		10	17	17	1,71
Be	0,1		0,001	0,004		0,5	0,59		9	13	11	0,05
B			0,051	0,169		0,3	0,48			26	26	0,07
Sc			0,012	0,040	17,00	3,5	4,22	20,4		11	9	0,31
Co	0,5	0,037	0,002	0,006		10,4	12,17		10	8	7	0,69
Ni	0,2	0,701	0,104	0,348	34,00	19,8	23,77	58,4	10	8	7	1,32
Cu	0,5	0,585	0,125	0,415		31,3	39,71		9	8	6	1,90
Zn	2	5,717	0,467	1,557		22,4	24,67		19	14	10	2,28
Ge		0,066	0,002	0,008		0,1	0,10			13	15	0,01
As	0,1	0,087	0,002	0,007		1,2	1,25		0.1	7	6	0,07
Se	0,5	0,302	0,021	0,068		0,1	0,08		46	45	167	0,05
Zr	0,5	0,083	0,004	0,015	410,77	7,8	11,08	1,9	8	11	9	0,65
Nb		0,151	0,006	0,021	14,38	1,3	1,08	9,0		48	44	0,70
Mo	0,05	0,234	0,003	0,009		0,3	0,30		6	10	7	0,02
Ag	0,02	0,005	0,007	2,33		0,04	0,04		12	13	14	0,005
Cd	0,01	0,210	0,002	0,006		0,03	0,03		12	10	9	0,003
Sn	0,1		0,002	0,007		0,3	0,31		7	25	11	0,03
Ba	4	0,981	0,101	0,338	683,13	80,7	95,60	11,8	12	7	6	5,05
Pr		0,051	0,821	2,74	11,42	4,2	5,12	37,2		11	9	0,36
Nd		0,193	4,953	16,51	43,46	16,3	17,97	37,6		11	9	1,42
Sm		0,019	0,686	2,29	8,54	2,7	3,25	32,1		9	8	0,21
Eu		0,012	0,248	0,83	1,98	0,5	0,63	26,8		9	8	0,04
Gd		0,031	1,604	5,35	7,30	3,0	3,34	40,4		9	9	0,26
Tb		0,006	0,119	0,40	1,18	0,3	0,39	27,8		9	8	0,03
Dy		0,078	0,333	1,11	7,08	1,6	1,92	23,1		10	8	0,12
Ho		0,005	0,139	0,46	1,42	0,3	0,36	21,7		10	8	0,02
Er		0,010	0,588	1,96	3,96	0,9	1,03	22,3		10	8	0,07
Tm		0,003	0,086	0,29	0,58	0,1	0,13	18,5		10	8	0,01
Yb		0,018	0,404	1,35	3,69	0,7	0,83	18,9		10	9	0,06
Lu		0,023	0,127	0,42	0,57	0,1	0,12	17,4		10	9	0,01
W	0,02		0,007	0,022		0,1	0,10		14	74	32	0,02
Tl	0,02	0,011	1,210	4,02		0,1	0,14		5	7	7	0,01
Pb	1		0,009	0,028	9,23	4,6	4,92	50,3	6	7	6	0,30
Bi	0,01	0,198	0,520	1,72		0,0	0,05		8	9	30	0,02
Th	1		0,016	0,054	8,30	5,2	6,27	62,7	11	8	7	0,36
U	0,1	0,009	0,550	1,84	2,99	1,2	1,46	40,7	11	8	8	0,10

[1] Based on the standard deviation of method blank analyses

[2] Analysed at the WSU Geoanalytical labs, see Johnson et al. (1997) for method description

[3] Based on the average of 228 analyse

[4] Based on the average of 6 analyse

[5] From the ratio of partial leach to total concentration data using the MP2 standard

REFERENCES

JCGM, 2008: *Evaluation of measurement data - Guide to the expression of uncertainty in measurement*. Joint Committee for Guides in Metrology, 120p.

Johnson, D.M., Hooper, P.R. & Conrey, R.M., 1997: XRF analysis of rocks and minerals for major and trace elements on a single low dilution Li-tetraborate fused bead. *Advances in X-ray Analysis, 41*.

Lax K. & Selinus O., 2005: Geochemical mapping at the Geological Survey of Sweden. *Geochemistry: Exploration, Environment, Analysis* 5, 337–346.

MacDougall, D. & Crummett W.B., 1980: Guidelines for data acquisition and data quality evaluation in environmental chemistry. *Analytical Chemistry 52 (14)*, 2242–2249.

Naturvårdsverket, 1999: Metodik för inventering av förorenade områden. *Naturvårdsverket rapport 4918*.

Swedish Standards Institute, 1997: Soil Analysis – Determination of trace elements in soils – Extraction with Nitric Acid. Svensk Standard SS 02 83 11.

Thompson, M., Potts, P.J., & Webb, P.C., 1996: GeoPT1. International Proficiency Test for Analytical Geochemistry Laboratories - Report on Round 1 (July 1996). *Geostandards Newsletter 20(2)*, 295–325.