



**Sample treatment and analytical methods
used at Orkustofnun laboratory (1999)**

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Greinargerð HK-HÁ-KHS-JÖB-MÓ-StH-VH-99-07



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Water samples are collected in several fractions: Ru samples are untreated (raw). Samples meant for the analysis of pH and volatiles (CO₂, H₂S, NH₃) are collected in airtight gas bulbs or in Giggenbach flasks. Rd samples are raw and diluted samples for the analyses of silica. Samples for gas analysis are collected into evacuated Giggenbach flasks containing 50 ml of 10 M NaOH. Fu samples are filtered through 0.45 µm membrane filters but not treated in any other way. Fu samples for NO₃, NO₂ and NH₃ to be measured by autoanalyzer are filtered by 0.22 µm membrane filters. Fa samples are filtered and acidified by 1 ml concentrated "Suprapur" HNO₃ added to 500 ml sample. Fp samples are filtered and added zink acetate to precipitate sulfide to prevent its oxidation to sulfate.

Analytical methods are briefly compiled in the table below. Besides the handbooks for each instrument the methods are mainly based on the following references: EPA Methods for Chemical analysis of Water and Wastes, United States Environmental protection Agency, Office of Research and Development, Washington D.C. EPA/600/4-79/020 March 1982; Keith L.H. (editor) 1992: Compilation of E.P.A.'s Sampling and Analytical Methods, Lewis Publishers Inc., Celsea, MI, 803 pp; Franson, M.H. (editor) 1980: Standard Methods for the Examination of Water and Wastewater, 15th Edition, American Public Health Association, Washington D.C., 1134 pp; Grasshoff, K., Erhardt, M. and Kremling K. 1983: Methods of Seawater Analysis 2nd Edition, Verlag Chemie, Weinheim, 419 pp; Trujillo, P.E., Counce, D., Grigsby, C.O., Goff, F and Shevenell, L. 1987: Chemical Analysis and sampling Techniques for Geothermal Fluids and Gases at the Fenton Hill Laboratory, Los Alamos National Laboratory LA-11006-MS, 84 pp; Ólafsson, M. 1988, Sampling Methods for Geothermal Fluids and Gases, Orkustofnun, OS-88041/JHD-06, 17 pp.

Compilation of analytical methods

Constituent	Fraction	Method	Brief description	Standard	RSD%	D.1. (µg/l)
pH	Ru	Electrometric	A glass electrode combined with a reference potential is inserted into the sample, pH and temperature values recorded.	Merck titrisol, pH 4, 7, 10	±0.1 pH unit	
Conductivity	Fu	Bridge	Specific conductance is measured using a Wheatstone type bridge using temperature compensation to 25 °C.	KCl	±5µS/cm	
Tot. carb. as CO ₂	Ru	Electrometric titration/titration	Sample pH adjusted to 8.2 with HCL/NaOH, then titrated to pH 3.8 with 0.1N HCL using a pH meter.	Merck titrisol 0.1N HCL	3.6 for 5-1500 ppm	1000
H ₂ S	Ru	Titration	NaOH added to make sample basic. Titrated with 0.001 M HgAc, dithizone as indicator.		3.9 for 0.03-800 ppm	20
O ₂	Ru	Colorimetric	Measurements with chemmetric ampules.			1
SiO ₂	Rd	Spectrophotometry	Iodine and thiosulphate added to destroy H ₂ S, ammonium heptamolybdate and HCL added. Absorption determined at 410 nm.	Spóastadir thermal water, SiO ₂ conc. (104 ppm) determ. gravimetrically.	1.8-2.5 for 0.87-67.3 mg/l	500
F	Fu	Selective electrode	TISAB buffer added, electrode inserted and potential read.	Merck 1000 mg NaF/H ₂ O	3.5 for 0.85 ppm	2
Cl	Fu	IC	Anions from a small volume of samples are separated by means of a guard column, a separator column and a suppressor column. Cl determined using a conductivity detector.	Merck titrisol HCl/H ₂ O	2.9 for 10 mg/l	25
I	Fu	IC	Anions from a small volume of samples are separated by means of a guard column, a separator column. I is determined by using amperometric detector and using silver electrode.	KI	0.05	1
Br	Fu	IC	Anions from a small volume of samples are separated by means of a guard column, a separator column and a suppressor column. Br determined using a conductivity detector.	Merck titrisol BrCl/H ₂ O	9 for 0.05	50
SO ₄	Fu/Fp	IC	Anions from a small volume of samples are separated by means of a guard column, a separator column and a suppressor column. SO ₄ determined using a conductivity detector.	Merck titrisol H ₂ SO ₄ /H ₂ O	1.5 for 98.5 mg/l	20
B	Fu	Spectrophotometry	Sample buffered with NH ₄ Ac/Na ₂ EDTA/ HAC Azomethine - H/ascorbic acid reagent added. Absorption determined at 420 nm.	Merck titrisol H ₃ BO ₃ /H ₂ O		5
Na	Fa	AAS DA	Small amount of Cs solution added and sample directly aspirated into oxidizing air acetylene flame. Absorption read at 589.6 nm.	Merck titrisol NaCl/H ₂ O	1.2-1.5 for 8.2-52 mg/l	1
K	Fa	AAS DA	Small amount of Cs solution is added and the sample directly aspirated into an oxidizing air acetylene flame. Absorption read at 766.5 nm.	Merck titrisol KCl/H ₂ O	7.9 -12.5 for 1.6-6.3 mg/l	1
Mg	Fa	AAS DA/AAS GF	A small amount of La solution is added to water sample which is directly aspirated into an oxidizing air-acetylene flame. Absorption read at 285.2nm	Merck titrisol MgCl ₂ /HCl	2.4-4.8 for 21-82 mg/l	1

Ca	Fa	AAS DA	A small amount of La solution is added and the sample directly aspirated into an oxidizing air acetylene flame. Absorption read at 422.7 nm	Merck titrisol CaCl ₂ /HCl	1.7-3.3 for 9.36 mg/l	10
Al	Fa	AAS GF	Dried 30 s 125°C, ashed 30 s 1500°C, atomized 3 s 2400°C. Purge gas Ar 309.3 nm	Merck Al(NO ₃) ₃ 0.5M HNO ₃		1
Fe	Fa	AAS GF	Dried 30 s 140°C, ashed 30 s 1200°C, atomized 3 s 2100°C. Purge gas Ar 248.3 nm	Merck Fe(NO ₃) ₃ 0.5M HNO ₃		0.1
Mn	Fa	AAS GF	Dried 30 s 140°C, ashed 30 s 1200°C, atomized 3 s 2400°C. Purge gas Ar.279.5 nm	Merck Mn(NO ₃) ₃ 0.5 M HNO ₃		0.1
Cu	Fa	AAS GF	Dried 30 s 125°C, ashed 30 s 900°C, atomized 2 s 2000°C. Purge gas Ar.324.7 nm	Merck Cu(NO ₃) ₂ 0.5 M HNO ₃		0.1
Zn	Fa	AAS GF DA	Dried 30 s 125°C, ashed 30 s 1200°C, atomized 3 s 2300°C. Purge gas Ar.357.9 nm	Merck Zn(NO ₃) ₂ 0.5 M HNO ₃	34-37 for 280-310 µg/l	0.1
As	Fa	AAS HG	Organic matter convert. with HNO ₃ -H ₂ SO ₄ -HClO ₄ . As reduced and converted to AsH ₃ using NaBH ₄ . The hydride swept into a heated cell in the beam of an As EDL lamp and As determined at 193.7 nm.	Merck H ₂ AsO ₄ 0.5 M HNO ₃	5.5-9 for 5-20 µg/l	0.1
Cr	Fa	AAS GF	Dried 30 s 125°C, ashed 30 s 1200°C, atomized 3 s 2300°C. Purge gas Ar.357.9 nm	Merck Cr(NO ₃) ₃ 0.5 M HNO ₃	0.4-1 for 19-77 µg/l	0.1
Pb	Fa	AAS GF	Dried 30 s 125°C, ashed 30 s 750°C atomized 2 s 2000°C. Purge gas Ar. 283.3nm	Merck Pb(NO ₃) ₂ 0.5 M HNO ₃	3.2-5.2 for 25-100 µg/l	0.1
Li	Fa	AAS DA AES	Sample directly aspirated into an oxidizing air-acetylene flame. Absorption read at 670.8 nm. Clay digests aspirated into air-acetylene flame and emission read at 670.8 nm.	Merck titrisol for 0.1 ppm. Na, K and Li after dilution to 1 l		0.5
Hg	Fu	AAS F1	Hg is reduced and converted to HgH ₂ with NaBH ₄ . Hydride is swept into a cell, placed in beam of an Hg EDL lamp and atomic abs. determ. at 2573.7 nm. At collection KMnO ₄ / K ₂ S ₂ O ₈ / HNO ₃ added to water sample, At start of determ. H ₂ NOH, HCl and SnCl ₂ added. The resulting gaseous Hg is amalgamated with gold and heated to be released into a cell for flameless AAS determ. at 253.7 nm	Merck Hg(NO ₃) ₂ 0.5 M HNO ₃	4-16 for 2.5-18.1 ng/l	0.001
CO ₂	Gigg	Electrometric titration	CO ₂ is collected into the 10 M NaOH solution in the Giggbach flask and determined by pH titration: 2 ml of sample is diluted to 50 ml, pH is adjusted to 8.2 with HCl/NaOH, then titrated to pH 3.8 with 0.1N HCl using pH meter. Blank contribution is subtracted.		3.6 for 5- 1500 ppm	1000
H ₂ S	Gigg	Titration	H ₂ S is collected into the 10 M NaOH solution in the Giggbach flask and determined by titration :NaOH is added to make sample basic. Titrated with 0.001 M HgAc, dithizone as indicator.		3.9 for 0.03- 800 ppm	20
CH ₄	Gigg	Gas chromatograph	Thermal conductivity detector. H ₂ carrier gas.		2 %	
H ₂	Gigg	Gas chromatograph	Thermal conductivity detector. N ₂ carrier gas.	Pure hydrogen gas	2 %	
O ₂ +Argon	Gigg	Gas chromatograph	Thermal conductivity detector. H ₂ carrier gas	Atmospheric air	2 %	
TDS	Fu	Gravimetric	Sample evaporated and dried at 105°C		2.6-3.8 for 190-1680 ppm	2500

Abbreviations:

AAS	= Atomic absorption spectroscopy	DA	= Direct aspiration
GF	= Graphite furnace	D.l.	= Detection limit
Fa	= Filtered, acidified	Ru	= Raw, untreated
Fu	= Filtered, untreated	RSD	= Relative standard deviation
Fp	= Filtered, precipitated	Rd	= Raw, diluted
Gigg	=Giggbach flasks		