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Total Silica Analysis Using a Double Beam Atomic Absorption Spectrophotometer

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ABSTRACT

Total silica in geothermal brine when diluted to concentrations less than 100 mg/l and acidified to pH 2.0 or less right after sampling will remain in solution as monomeric silica (Iler, 1978). Experimental runs using atomic absorption spectrophotometry (AAS) in analyzing total silica from geothermal brine was done at Southern Negros Geothermal Production Field (SNGPF) laboratory since 1998. The results were then compared with runs using UV-Visible spectroscopy, which is the standard method adopted by all PNOC-EDC laboratories. This study aims to obtain percent difference of less than 5% with the colorimetric method (UV-ViS) in terms of ppm result. Comparatively the alternative method is cheaper and faster compared with the traditional technique. Repeatable results can be obtained within several minutes to an hour upon sample receipt. Between 2002 to 2003 SNGPF laboratory have used the method of AAS for analyzing total silica. The method was also used in the 2003 IAEA water inter-lab consisting of medium and highly saline brine waters. The results passed for both water types. Optimum instrument settings and stable current is a must for attaining quality results.

1. INTRODUCTION

The silica concentrations of the brine are the basis for widely used chemical geothermometers; silica concentrations are also required in the assessment of the scaling potential in pipelines. Concentrations can range up to 1200 mg/kg SiO_2, but are normally <700 mg/kg. The present analysis of silica at PNOC-EDC laboratories uses the colorimetric technique, which has a very good precision and accuracy up to ±3%. This method however requires longer preparation time of samples and requires the ammonium heptamolybdate chemical as its main reagent for the development of the yellow molybdic acid. The precision of the method is based largely on the experience and speed of the analyst since the yellow color degrades rapidly during development. It also requires a digestion of at least 45 minutes to an hour at 90ºC in caustic solution. On the other hand, the AAS method measures total silica from acidified and filtered samples without any caustic digestion. The sample preparation time is significantly shorter and silica results can be obtained within a few minutes to an hour. There is no need to use the ammonium heptamolybdate reagent which contains the heavy metal Molybdenum. Only acidified distilled water and class A volumetric pipettes are used for diluting the samples.

2. REAGENTS

Silicon Standard Solution, 1000 mg/L commercial AAS standard.

3. SAFETY

Operation of an atomic absorption spectrometer involves the use of compressed gases, flames and hazardous materials including corrosive fluids and flammable liquids. Unskilled, improper or careless use of the instrument can create explosion hazards, fire hazards or other hazards which can cause death, serious injury to personnel, or severe damage to equipment and property.

4. APPARATUS / EQUIPMENT

1. GBC906 AAS equivalent or latest models.

2. Exhaust Vent/Fume hood – this will protect laboratory personnel from toxic vapors which may be produced. It also improves the stability of the flame and tends to remove the effects of room drafts and the laboratory atmosphere. It helps protect the instrument from corrosive vapors.

3. Compressor – supplies compressed air requiring a minimum air pressure of 412 kPa (60 psi). It is desirable to have a water and oil trap between the compressor and the burner-nebulizer gas control box to keep oil and water droplets out of the flow metering system. The pressure of air supplied to the burner should be at least 20 psig greater than the N_2O pressure.

4. Acetylene the preferred fuel gas with any atomic absorption equipment. This is normally supplied dissolved in acetone. The acetylene cylinder should be replaced when the cylinder pressure drops to about 600 kPa (85 psig). Cylinder tanks should be stored and operated in a vertical position, rather than horizontally, to prevent liquid acetone from reaching the cylinder valve.

5. Nitrous Oxide When refractory elements are to be determined, the high temperature combination of nitrous oxide and acetylene is required. When nitrous oxide is rapidly removed from the cylinder, the expanding gas causes cooling of the cylinder pressure regulator and the regulator diaphragm so that it sometimes freezes. This can create erratic flame conditions or, in the most extreme case, a flashback. It is therefore advisable to heat the regulator, using either a built-in heater or an externally supplied source of heat such as an electrical resistance heating tape.

6. A nitrous oxide burner made of titanium with burner head interlock

7. Drain Vessel. A vessel to gather the effluent should be made of plastic and have a fairly wide mouth.

Neutral solutions of silica in seawater containing about 1 ppm SiO_2 can lose silica on standing in polyethylene bottles, but there was no loss at low pH. It was thought that this could have been caused by adsorption of silica by the plastic at neutral pH. It is more likely caused by aggregation and settling owing to traces of metals such as Aluminum, Magnesium in seawater. No such interaction occurs at low pH.

Severe depression of silicon absorbance has been observed in the presence of HF, H_3BO_3, and K^+ at significant levels (1%). The effect is minimized by adjusting the flame to neutral stoichiometry (red cone 0.5 – 1 cm high) with consequent loss of sensitivity.

The method is applicable to all waters including geothermal brine and steam condensate. The detection limit is 20.0 mg SiO_2/L. Either silica or silicon standard can be used in the analysis.

5. PROCEDURE

1. Sample Treatment and Holding Time. Vacuum filter sample through 0.45µm membrane filter immediately upon receipt. Acidify with 3.0 ml of 1:1 Nitric acid per 1L of filtrate.
2. Pipet 5 ml sample aliquot and dilute to volume with acidified distilled deionized (DD) water into 100 ml volumetric flask.
3. Pipet 5 ml, 10 ml, 15 ml, 20 ml, 25 ml standard from a 100 mg SiO_2/L intermediate standard into separate 50 mL volumetric flasks. Dilute to mark with acidified DD water. If using a Si standard titrisol this is equivalent to 21.4, 42.8, 64.7, 85.6 and 107 ppm silica working standards.
4. Optimize the atomic absorption spectrophotometer.
5. Check the air line filter, especially if there is an excessive amount of sodium emission in the flame (yellow flicks).
6. Make sure the capillary and the nebulizer hole is not blocked. Also ensure proper positioning of the lamp in the lamp turret or lamp holder. Align the burner horizontally and vertically.
7. Use only clean nitrous oxide burner during standard and sample runs. Warm up the burner while aspirating a blank solution for 3 to 5 minutes.
8. Adjust the absorbance reading of the highest concentration standard, i.e. 107 ppm to around 0.10 absorbance unit or more.
9. Run the calibration standards starting from the lowest concentration standard. Run the samples once the linear regression coefficient (r^2) of 0.999 is attained (LPM, 1999).
10. Run a standard blank before standard calibration. Start the sample run with a sample blank then run a control standard (107 ppm SiO_2).
11. After 10 sample runs run a sample blank, a check standard preferably that standard nearest to the sample concentration range. Also run a duplicate sample.

6. CALIBRATION CURVE

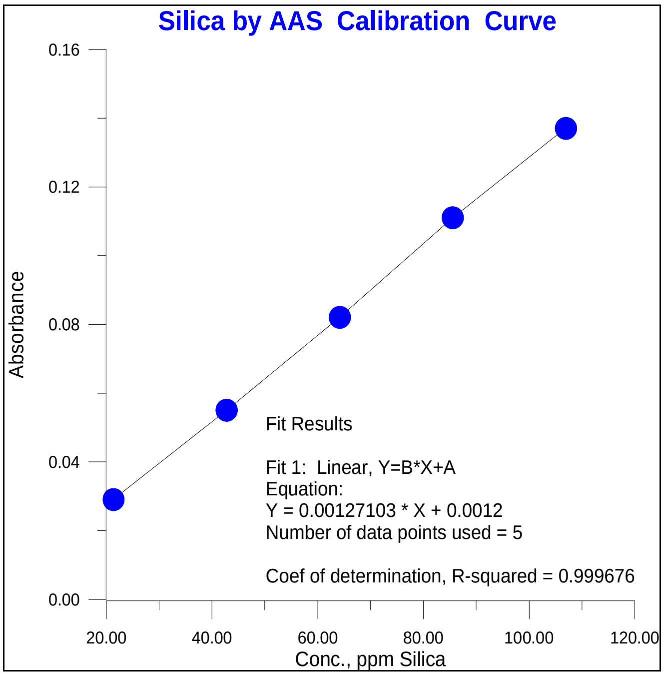

Figure 1. Calibration curve of Silica analysis by AAS.

Table 1 Calibration table of SiO_2 by AAS

Silica conc., mg/L	Absorbance
21.4	0.029
42.8	0.055
64.2	0.082
85.6	0.111
107	0.137
r^2	0.99968

A low concentration set of standards is used so that samples have to be diluted 10-20x prior to reading. This eliminates matrix effects and ensures that silica concentration is less than 100 mg/L in solution. At this concentration silica exists in the monomeric form. (ILER, 1978)

Verma and Santoyo performed a statistical analysis of the IAEA data and found that the analytical uncertainty for silica increases with increasing concentrations. (Proceeding Stanford Geothermal Workshop, 2002) Verma et al. also performed an inter-laboratory calibration using commercial standard as samples and found similar results. They described the reasons for getting higher analytical errors for high concentration silica samples. (Geothermics, vol 31, 2003)

7. INTERLABORATORY RESULTS

In 2002 an inter-laboratory comparison of two water samples of high and low level salinities was organized by PNOC-EDC among geothermal laboratories in the Philippines. The participating laboratories are the five laboratories of PNOC-EDC, the two laboratories of Philippine Geothermal Inc. (PGI) and the chemistry laboratory of Philippine Department of Energy (DOE) Energy research laboratory. Of the eight (8) laboratories that participated only three laboratories consisting of SNGPF, PG-Makban and PGI-Tiwi chemistry laboratories used the AAS for analyzing total silica while the rest of the laboratories used the conventional colorimetric or Molybdosilicate method. The final accepted mean for the high salinity brine is 601 ppm silica for sample ILP-02-01 while the final accepted mean for the low salinity water is 96.9 ppm silica. The three laboratories using the AAS method got the following results:

Table 2 2002 IAEA interlaboratory results for Silica analyzed by AAS. Only SNGPF(PNOC lab), PGI-Makban, and PGI-Tiwi used the silica by AAS method. S.D. = standard deviation; %RSD = % Relative standard deviation.

Sample	SNGP	Makban	Tiwi	Mean	S.D.	%RSD
ILP-02-01	594	600	573	589	14	2.41
ILP-02-02	98	95	99.73	97.6	2.4	2.45

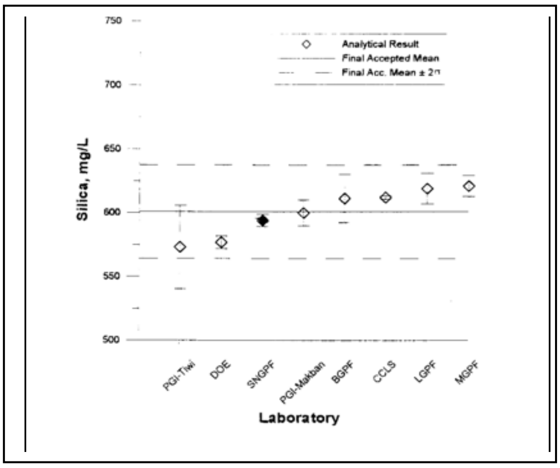

Figure 2. Silica results of the participating laboratories for the 2002 water inter-laboratory comparison, ILP-02-01.

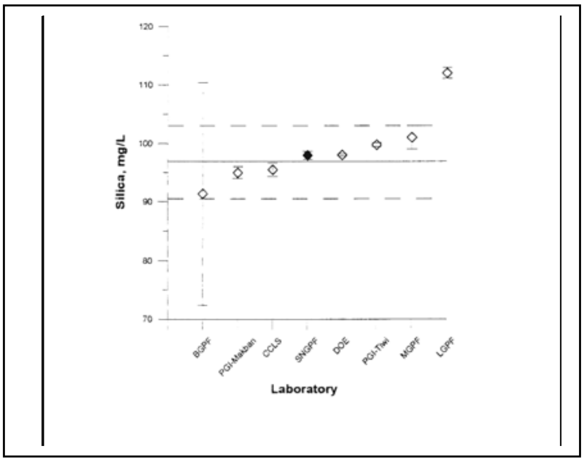

Figure 3. Silica results for ILP-02-02 sample. Note that SNGPF result is in the middle while one laboratory using the colorimetric method is outside the ±2 sigma range.

In 2003 an inter-laboratory comparison was headed by IAEA in which a total of 31 laboratories participated. The samples are GW-03-01 and GW-03-02 consisting of high and low salinity fluids respectively. Of the 31 laboratories only 9 laboratories used AAS for analyzing total silica.

Table 3 2003 IAEA water inter-laboratory comparison. Silica results for laboratories using the AAS method. The outliers* are not included in the computation of the statistics.

Laboratories	GW-03-01	GW-03-02
1. Code R3	224.3	479
2. SNGPF P12	222	529
3. Code P2	210.2	470
4. Code P5	217	477
5. Code P7	208	471
6. Code P15	213	498
7. Code P18	226.85	500
8. Code P24	250.36	541*
9. Code P25	255.4*	688*
Mean	221.4	489
Standard Deviation	13.48	21.33
% RSD	6.09	4.36

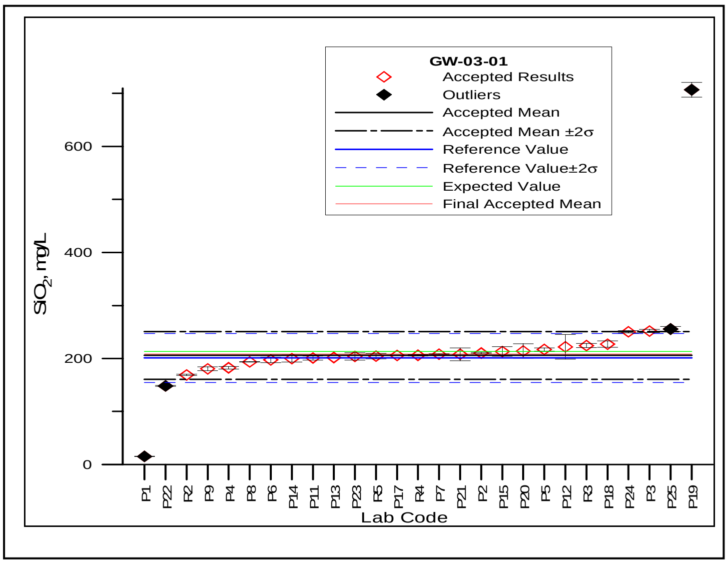

Figure 4. IAEA water inter-lab results for silica analyses. This graph shows all the silica results for GW-03-01 sample. The laboratories using the AAS method are found in table 3

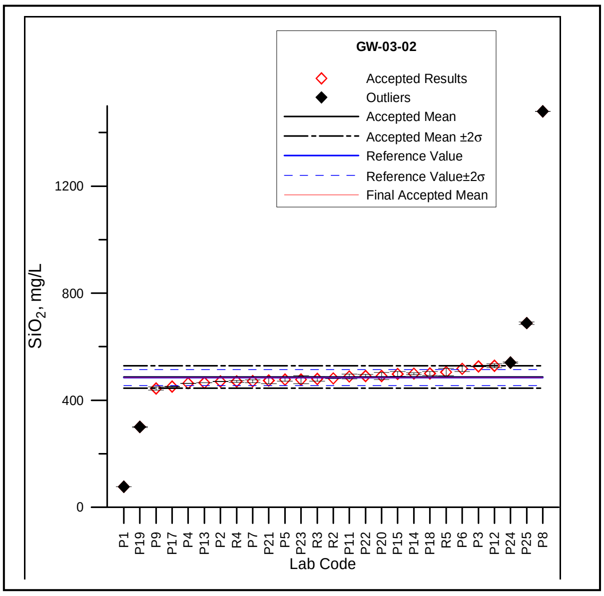

Figure 5. 2003 IAEA water interlab. Silica results for GW-03-02

8. RUGGEDNESS TEST

Ruggedness testing is a procedure wherein the analytical method is evaluated whether it is rugged or sensitive to minor variations in some of the analytical parameters. Usually it is best to select a rugged type of analytical method. Ideally, in-house methods adopted in the laboratory should be subjected to this kind of test before being accepted (Aragon, 2004). A procedure for ruggedness testing is available from a book by James P. Dux entitled “Handbook of Quality Assurance for the Analytical Chemistry Laboratory” (Dux, 1998). This technique is also called the Youdden Ruggedness test where the effect of seven variables can be determined by doing only eight analysis. (Aragon, 2004)

1. Storage (A) – Filtration is done within 24 hours upon sampling; against (a) – Filtration is done 2 weeks upon sampling.

2. Pore size of Filter Paper (B) – use of Whatman#4; against (b) – use of 0.45µm filter paper

3. Dilution (C) – 20x against (c) – 40x

4. Fuel/Oxidant ratio (D) – 7.0 / 8.5 against (d) – 8.0 / 8.5

5. Acetylene pressure (E) – 10 psi against (e) – 13 psi

6. Preset absorbance of highest standard (F) ≤ 0.10 absorbance for 107 ppm SiO_2 standard against (f) >0.10 absorbance for 107 ppm SiO_2 standard

Table 4 The Youdden Ruggedness Test Design by GMA

Factor Value	Combination or analysis number							
	1	2	3	4	5	6	7	8
A or a	A	A	A	A	a	a	a	a
B or b	B	B	b	b	B	B	b	b
C or c	C	c	C	c	C	c	C	c
D or d	D	D	d	d	d	d	D	D
E or e	E	e	E	e	e	E	e	E
F or f	F	f	f	F	F	f	f	F
Results	s	t	u	v	w	x	y	z

Table 5 SNGPF analytical results

No.	Treatment	Trials/Replicates				
		1	2	3	4	Mean
1	Colorimetric	1149	1150	1160	1150	1152
2	ABCDEF	1299	1254	1272	1164	1247
3	ABcDef	1173	1127	1124	1208	1158
4	AbCdEf	1212	1149	1208	1214	1196
5	AbcdeF	1230	1272	1275	1216	1248
6	aBCdeF	1213	1226	1225	1211	1219
7	aBcdEf	1246	1253	1026	1309	1209
8	abCDef	1184	1167	1210	1192	1188
9	abcDEF	1239	1114	1172	1243	1192

Table 6 Evaluation of Results. % Diff. = (upper-lower case) / mean of colorimetric x 100

Variable	Ave. of Upper Case	Ave. of Lower Case	% Difference
1	1212	1202	0.9%
2	1208	1206	0.2%
3	1213	1202	0.9%
4	1196	1218	-1.9%
5	1211	1203	0.7%
6	1227	1188	3.4%

For SNGPF laboratory (Palinpinon) as well as for LGPF laboratory (Tongonan), the silica by AAS method turned out to be rugged. The older types of AA spectrophotometers have a disadvantage due to the N_2O burner design. It has a flat and even surface so that carbon deposits easily accumulates besides the burner opening after several runs. Careful attention to sampling treatment like acidification with 10 ml (1+1) Nitric acid per 500 ml of sample should be done as soon as the sample is collected. Acidified samples are then filtered within 24 hours upon receipt and diluted ten to twenty times with acidified distilled and de-ionized (DD) water. Sample analysis is preferably done right after dilution or within the next 24 hours or so.

9. STANDARD RUN AS SAMPLES

Table 7 Standard concentrations run as samples using AAS vs.UVViS.

Standard Conc.	AAS	ppm Diff.	UVVis	ppm Diff.
214	221	-7	211	3
	238	-24	210	4
428	425	3	435	-7
	444	-16	439	-11
856	872	-16	860	-4
	860	-4	858	-2
1284	1297	-13	1275	9
1284	1250	34	1279	5

The results taken from recent runs at SNGPF Geoscientific Chemistry laboratory showed that the analytical values for silica concentration at the range of 856 ppm and below showed a minimal difference with the colorimetric technique. With silica concentrations above 1000 ppm the difference between the two methods is quite significant. These data are done at 10x dilution. In Verma et al. 2002 (Geothermics vol.31) it was observed that the dilution technique is better than direct injection of high concentration samples to the atomic absorption spectrometer.

10. DISCUSSION

Atomic absorption techniques have become the preferred method of elemental analysis. Ideally, standards for atomic absorption determination should closely resemble the sample in terms of overall composition. The analyte (acidified sample) should have a pH range of 1.0–2.0 pH units. To slow down polymerization of silica, the samples are diluted ten to twenty times. A calibration curve ranging from 20 to 100 ppm silica is prepared. It should have a linear regression coefficient of at least 0.999. In the atomic absorption method the equipment represents a large investment, but once the samples have been prepared in solution, permits dozens of samples to be run in a few hours. This method determines total silica, and does not distinguish between soluble and insoluble forms. No complexing agent is added like the ammonium molybdate used in the colorimetric method. The most important aspect to remember is that the nitrous oxide-acetylene flame should be reducing with a 50 mm high red zone.

11. CONCLUSION

Based on previous experience and considering the ruggedness test on silica by AAS conducted by PNOC-EDC laboratories, the optimum working range of silica analyzed as Si is between 20-100 mg/L. This gives an equivalent absorbance of 0.023 to 0.119 absorbance units respectively. No ionization suppressants are needed. The minimum dilution for a silica concentration of about 700 mg/L is ten times. Good linearity is obtained with an r^2 equivalent to 0.9995. The percent recovery of the spiked sample range from 95-99%. The percent difference of the check and control standards range from 0.50 to 4.3 %. A comparison was made between the AAS method against the UV Visible spectroscopy. After excluding outliers and using the student t-test statistic, no significant difference was noted. The difference in mg/L range from 3-28 mg/L.

This study proved that with thorough knowledge and proper optimization of the instrument, silica in geothermal brine can be analyzed using flame AAS. The results of this method are also comparable with the colorimetric method. Total silica analysis by AAS is an alternate method, which is simpler, more direct, and offers a significantly faster analysis compared to the conventional yellow molybdate (colorimetric) method.

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REFERENCES

Analytical Chemistry Principles and Techniques, Hargis, L.G., 1988

Analysis of Geothermal Waters and Gases, Committee on Standardization of Analytical Methods, 1988, PNOC-EDC, Geoscientific department.

An assessment of the results of the IAEA inter-laboratory comparisons for geothermal water chemistry, Proceedings Twenty-Seventh Workshop on Geothermal water chemistry. Proceedings Twenty-Seventh Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, California, pp. 436-443.

An interlaboratory calibration of silica for geothermal water chemistry, Verma, Mahendra P., Tello, Enrigque, Sandoval, Fernando, Tovar Rigoberto, Martinez, Jose Luis, Geothermics vol. 31, Issue 6, December 2002.

Collection and Analysis of Geothermal and Volcanic Water and Gas Discharges, Report No. CD2401, 4th Edition, Giggenbach, W.F. and Goguel, R.L., Oct. 1989, DSIR, Petone, N.Z.

Dux, J.P. Handbook of Quality Assurance for the Analytical Chemistry Laboratory, Second Edition, 1998.

Flame Atomic Absorption Spectrometry Analytical Methods, Varian Publication No. 8510000900, Varian Australia Pty Ltd 679 Springvale Road Mulgrave VIC 3170.

Flame Methods Manual for Atomic Absorption, GBC Scientific Equipment Pty Ltd., P.N. 01-0019-00

Laboratory Procedures Manual (LPM), SNGPF Chemistry Laboratory, 1999

Recommended Practice Guidelines for the Purity and Handling of Gases Used in Atomic Absorption Spectroscopy, Scientific Apparatus Makers Association, 1140 Connecticut Avenue, N.W., Washington, D.C. 20036

Ruggedness Testing of Silica Analysis by Atomic Absorption Spectrophotometry, G.M. Aragon, Feb. 2004, PNOC-EDC unpublished report.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, APHA-AWWA-WEF, 1998

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The Chemistry of Silica, Solubility, Polymerization, Colloid, and Surface Properties, and Biochemistry", Iler, R.K.

Test Method for Low-level Total Silica in High Purity Water by Flameless Atomic Absorption Spectroscopy, Vol. 11.02, D4517-85 (1990), Annual book of ASTM Standards, 1994, p697.