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An interlaboratory calibration of silica for geothermal water chemistry

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Abstract

The results of an interlaboratory calibration of silica performed using commercial standards as samples are presented. The analytical values for silica concentration are consistent for lower concentration samples, but there are significant variations among the values for the higher concentration samples. The dilution technique is better than direct injection of high concentration samples to the atomic absorption spectrometer, although at present it is not possible to define the highest permissible silica concentration appropriate for direct measurements. High dilution factors also produce a high uncertainty in the analytical results. Therefore, the need still exists for conducting multi-laboratory calibrations over a wide range of silica concentrations to refine the precision and accuracy of silica analyses at high concentrations.

Keywords: Geothermal fluid; Silica; Calibration; Atomic absorption spectrometry; Colorimetry

1. Introduction

High quality analytical data of separated water and vapor are of fundamental importance in the geochemical modeling of hydrothermal systems. Very little work has however been done to evaluate the uncertainty of the results related to analytical errors. To ensure the analytical quality of geochemistry laboratories, Ellis (1976)

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conducted the first interlaboratory comparisons of chemical analyses of geothermal waters involving many different countries. The scatter in the results he obtained revealed serious deficiencies in analytical accuracy and the need for general improvement and standardization of analytical procedures (Giggenbach et al., 1992). Consequently, in 1985 the International Atomic Energy Agency, Vienna (IAEA) initiated interlaboratory calibrations for geothermal waters within the framework of the project, "*Coordinated Research Program on the Application of Isotope and Geochemical Techniques in Geothermal Exploration*". Since then, the IAEA has conducted four interlaboratory calibrations of pH, Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, F^-, B, As, and SiO_2, which were analyzed in geochemistry laboratories involved in geothermal development all over the world. Verma and Santoyo (2002) performed a statistical analysis of the data and concluded that for all of the chemical parameters except SiO_2, the analytical error increases with decreasing concentration and is of the same order of magnitude for concentrations of less than 1 ppm. Similarly, they suggested that there were some serious problems with the sampling and analytical procedures used for SiO_2 and HCO_3^-.

Silica chemistry is of vital concern in the geothermal industry for estimating deep reservoir temperatures and preventing silica scaling during production and reinjection of geothermal brines. Thus the need for good quality analyses is implicit.

Natural geothermal waters were distributed as samples during the IAEA interlaboratory calibration program. However, there are some limitations in using natural waters as samples for calibration. First, the exact concentrations of the dissolved chemical species in natural waters are not known precisely. In other words, the reference values for the concentration of each chemical species are unknown and consequently it is difficult to evaluate the analytical quality of the participating laboratories. Secondly, the natural geothermal waters may be supersaturated with respect to some minerals. The chemical composition of these samples may therefore change during transport and storage due to mineral precipitation or gas exsolution. These limitations could be avoided by using commercial standards with established composition as samples.

In this article, we present the first results of an interlaboratory calibration of SiO_2 using commercial standards as samples. The analyses were conducted among "Comisión Federal de Electricidad" (CFE) geochemistry laboratories at Los Azufres, Los Humeros and Morelia, Mexico to evaluate the reasons for the observed variations in the analysis of silica.

2. The IAEA interlaboratory calibration study

Table 1 presents the silica analyses of samples distributed under the IAEA interlaboratory calibration programs. Giggenbach et al. (1992) presented the calibration of three samples, but the third sample was associated with natural organic gas discharges. Only the first two samples are therefore included here. The number of participating laboratories varies in each calibration: (A) 22 laboratories from 19

Table 1
Results of silica analyses of the geothermal water samples distributed under the IAEA calibration program

	Giggenbach et al. (1992)		Gerardo-Abaya et al. (1998)		Alvis-Isidro et al. (1999)		Alvis-Isidro et al. (2000)	
Lab No.	IAEA1	IAEA2	IAEA3	IAEA4	IAEA5	IAEA6	IAEA7	IAEA8
1	150	596	53.4	831	550	174	91.00	748
2	**57**[a]	283	70[b]	670	556	177	97.69	798.3
3	149	588	51.63	444	564	187	128.40	951.11
4			**21.02**	102	539	168	96.60	768
5	**283**	234	**19.57**	339	554	178	96.60	780.1
6	142	29	51.57	118	555	175	98.00	772
7		8	57.57	897			96.00	783
8	185	683	49	723	568	180	91.50	739.37
9	154	647	64	766	546.7	168.7	115.00	960
10	141	481	55.33	737	536	170	92.15	914.74
11	144	110	50.33	731	159	179	95.30	792
12	146	135	51.8	103	143.95	151.267	97.60	802
13	134	497	48.2	675	550.9	180.8	**55.1**	546
14			49.13	193	**< 6**	**6.4**	75.40	240.6
15	146	590	48.1	103	621	186	88.53	792.33
16					570.6	203.4	96.90	816
17	152	610			186.6	224.84	99.22	788.19
18	130	175			241.9	**77.45**	76.69	633.17
19	146	105			460.73	215.45	92.00	743
20	160	580			668.75	187.25	93.00	792
21	25	52			662.6	179.9	96.30	798
22	143	582			755	206	97.33	809
23					271.56	**98.097**	120.40	281
24					343.29	176.94		
25							123.13	936.37
26					131	155	99.00	810
27							101.00	810
28							145	425
29							91.00	735
30							80.41	227.59
31							144.23	1274
32							103.00	806
33							79.00	700
34							98.00	1121
35							93.97	322.5
Mean	145.5	367.6	52.5	495.5	466.8	178.1	96.8	773.1
S.D.	7.7	247.5	4.4	294.3	182.3	13.0	12.0	147.2
No. of samples	14	19	12	11	23	19	31	30

[a] The bold values were removed before statistical analysis of the data was performed.

[b] The underlined values were the outlier according to first mean ± 2 S.D.

countries (Giggenbach et al., 1992); (B) 15 laboratories from 7 countries (Gerardo-Abaya et al., 1998); (C) 26 laboratories from 10 countries (Alvis-Isidro et al., 1999); and (D) 35 laboratories from 16 countries (Alvis-Isidro et al., 2000). The samples from Giggenbach et al. (1992) are renamed as IAEA1 and IAEA2, from Gerardo-Abaya et al. (1998) as IAEA3 and IAEA4, from Alvis-Isidro et al. (1999) as IAEA5 and

IAEA6, and from Alvis-Isidro et al. (2000) as IAEA7 and IAEA8. The silica was analyzed by colorimetry (CO), atomic absorption spectrometry (AA), inductively coupled plasma with atomic emission spectrometry (ICP–AE) and inductively coupled plasma with mass spectrometry (IPC–MS). In this study, we consider all the results equally probable.

Alvis-Isidro et al. (1999, 2000) only reported the analytical techniques used by the individual laboratory. For example, the samples IAEA5 and IAEA6 were analyzed by laboratories 14, 8 and 2 using CO, AA and ICP-AE, respectively. Similarly, the samples IAEA7 and IAEA8 were analyzed by laboratories 19, 10, 4 and 1 using CO, AA, ICP AE and ICP MS, respectively. The values obtained using ICP–AE are relatively close to the mean values; however the number of analyses is too small to endorse its application. Most of the silica analyses were performed using colorimetry and atomic absorption spectrometry. The spread in the concentration values for both the techniques is similar. In summary, it is not possible to justify the superiority of one technique over others.

There are two types of error in every measurement: *determinate (systematic) and indeterminate (random) errors* (Bevington, 1969; Box et al., 1978). The determinate errors are due to instrumental defects, reagent impurities, personnel errors, method errors, etc. Commercial standards were not distributed and analyzed during the IAEA interlaboratory calibrations, so it was assumed that every laboratory had appropriate and standardized techniques to measure each parameter. It has been well established by stable isotope interlaboratory calibrations that common calibration or repeating the same standards with samples produces quite consistent results (Parr and Clements, 1991). Random errors, which accompany every measurement, are due to non-permanent causes and include noise present in the measurement.

Prior to statistically analyzing the IAEA results, values that were out of trend were removed. These values are generally associated with a variety of errors such as misprints or mistakes made during the handling and analysis of the sample. The arithmetic mean and standard deviation (S.D.) of the remaining values were then computed. The values that fell outside the mean ± 2 S.D. were rejected, and after the removal of these outliers, the mean and S.D. of the remaining data were recomputed (Table 1).

The silica concentration data (Table 1) are plotted in Fig. 1. The sample pairs (IAEA1-IAEA2, IAEA3-IAEA4, IAEA5-IAEA6 and IAEA7-IAEA8) are plotted together to compare the data from each laboratory. In Fig. 1A and B, the analyses of higher concentration samples (IAEA2 and IAEA4) can be divided into two groups (marked with dotted ellipses). In Fig. 1C and D, there are systematic errors in the data from some laboratories (marked with ellipses); however, other laboratories have consistent analyses for low concentrations (<200 ppm), but the measurements for high concentrations (>500 ppm) are significantly different (marked with rectangles). In order to understand the reasons for these inconsistencies, it would be necessary to run some commercial standards together with the interlaboratory calibration samples at all of the laboratories.

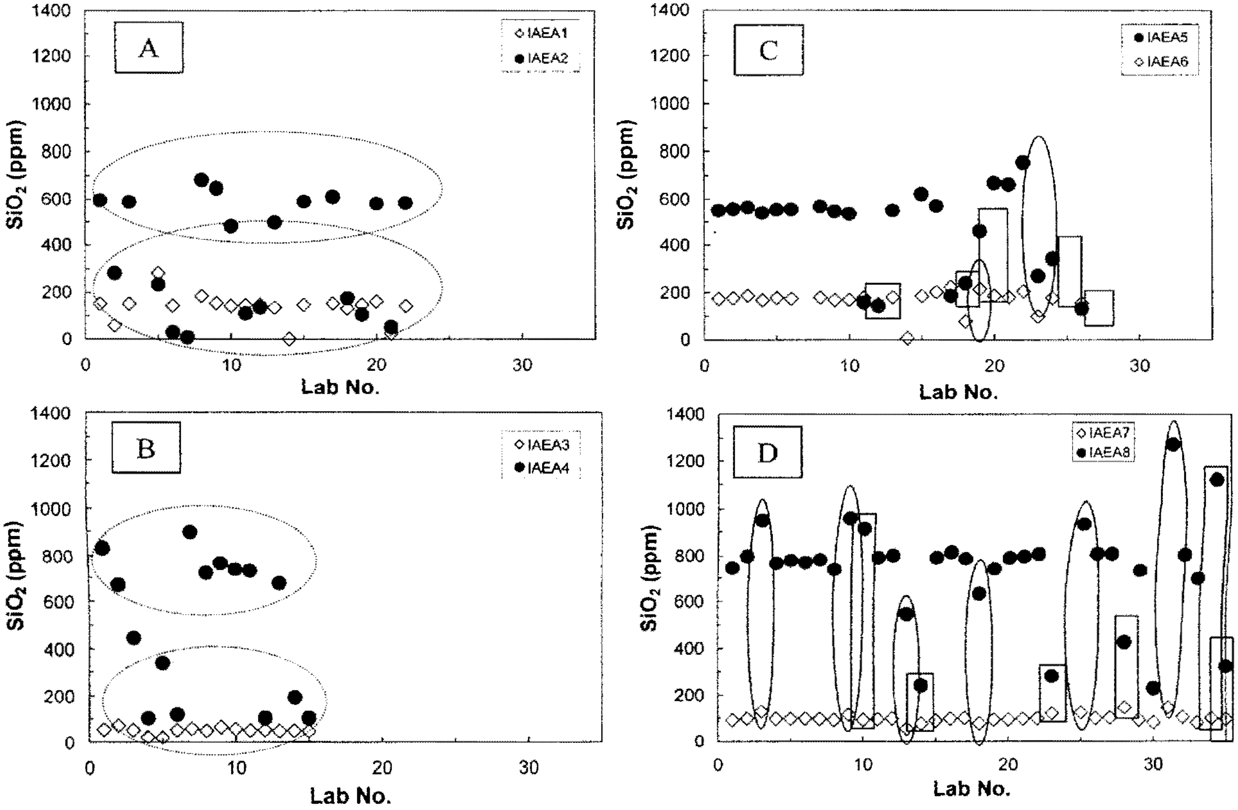

Fig. 1. Comparison of the IAEA interlaboratory calibration results of the silica analyses. The sample pairs (IAEA1-IAEA2, IAEA3-IAEA4, IAEA5-IAEA6 and IAEA7-IAEA8) are plotted together in order to compare the data from each laboratory. In Fig. 1A and B analyses of high concentration samples IAEA2 and IAEA4 can be divided into two groups outlined by the ellipses. In Fig. 1C and D, laboratories with systematic errors are denoted by ellipses; rectangles mark those with inconsistencies in high concentration samples only.

Table 2
The silica concentration data for each laboratory used to develop calibration curves

Lab I: AA		Lab II: AA Cal. 1		Lab II: AA Cal. 2		Lab IV: CO	
SiO_2 (ppm)	Msd Value	SiO_2 (ppm)	Msd Value	SiO_2 (ppm)	Msd Value	SiO_2 (ppm)	Msd Value
5	0.125	0	−0.0046	0	−0.0042	5	0.095
10	0.236	860	0.5695	43	0.0443	10	0.192
15	0.340	1074	0.7084	108	0.1240	20	0.384
20	0.438	1290	0.8886	172	0.2167	30	0.576
25	0.523	1720	1.1263	215	0.2872	40	0.772
		2151	1.3006	301	0.3848	50	0.931

AA, Atomic Absorption. CO, Colorimetry. Msd, measured.

3. Results of the interlaboratory calibration

Four commercial standards, prepared by diluting "9947 Titrisol silica standard, Merck, Germany", were distributed as samples among the three Mexican geochemical laboratories; one of the laboratories analyzed the samples by both AA and CO. The four sets of data are designated randomly as Lab I–IV. The samples were labeled in random order for each laboratory and the only information provided to the laboratories was the maximum expected silica concentration (2500 ppm).

Commercial silica standards are prepared with dissolving silicate or fluorosilicate minerals in alkaline solutions. The silica solubility in aqueous solutions increases exponentially above a pH of 8. Therefore, the commercial silica standards are substantially undersaturated at the ambient temperature and pH (>9). This means that the silica concentrations of the standards will be quite stable during transportation and storage.

Table 2 shows the internal calibration data used by the laboratories, except for Lab III, which did not provide its calibration data. The data are plotted in Fig. 2 with their corresponding linear regression equations. Lab II did not dilute the samples for the analyses. Therefore, there are two calibration curves for Lab II, one for lower concentration samples and another for higher concentrations. Similarly, Lab III also analyzed the samples without dilutions.

Table 3 presents the results of the measurements of the four samples, after internal calibrations, together with the real silica concentration. The error for each laboratory (1 S.D.) is calculated from the errors in the coefficients of the corresponding regression equation (Fig. 2) and the dilution factor. That is to say, the variations between the individual measurements of each sample were not taken into consideration in calculating the error. The reason for this is that the different laboratories measured the samples a different number of times. Furthermore, the error associated with individual measurements is not representative unless the number of measurements is sufficiently high (i.e. more than 5).

The results of the silica interlaboratory calibration (Table 3) are plotted in Fig. 3. Labs I and IV analyzed the samples after dilution, whereas Labs II and III analyzed

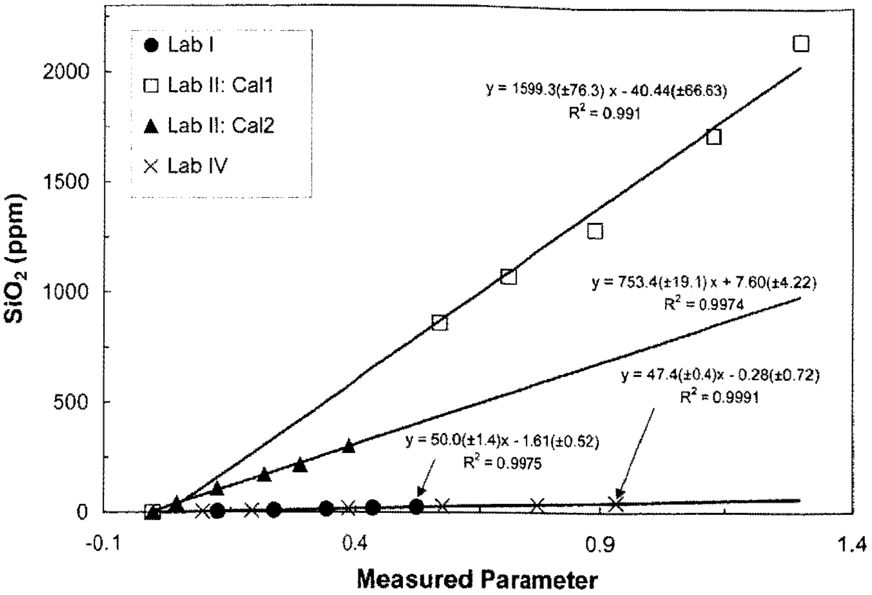

Fig. 2. The calibration curves for the different laboratories. Lab II used two calibration curves, Cal1 and Cal2 for low and high concentration samples, respectively.

Table 3
The silica (in ppm) calibration data

		Laboratory						Propagation of Error (1 S.D.)			
		I: AA		II: AA	III: AA	IV: CO		I: AA	II: AA	III: AA	IV: CO
Sample No.	Real values	Dilution factor	Value	Value	Value	Dilution factor	Value				
1	107	10	95	115	100	5	125	8	7		5
2	214	10	203	212	234	5	240	11	9		5
3	1071	50	925	1144	1238	50	1348	54	123		46
4	2143	100	2008	1745	1942	50	2549	112	152		55

without dilution. The values for lower concentration samples are on the 45° line for all the laboratories, whereas there is a wide dispersion among the higher concentration samples. The results are similar to the IAEA calibration data. Lab IV has a systematic positive error whereas Lab I has a systematic negative error. Values from Labs II and III have a random distribution.

Although the number of participating laboratories is low, it is clear that the injection of high concentration samples into the atomic absorption spectrometer produces higher random errors. It was found that there was some deposition on the flame slit that required frequent cleaning during analyses of these samples. Thus,

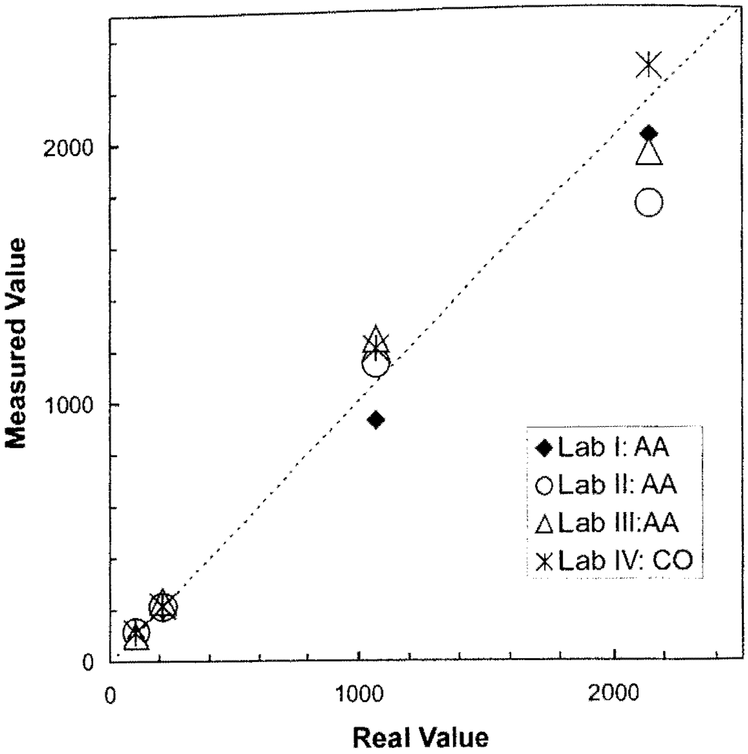

Fig. 3. Relationship between the real and measured silica concentrations. The analytical technique used by the individual laboratory is denoted by AA for atomic absorption spectrometry and CO for colorimetry.

there is a need to determine the maximum silica concentration in water samples that can be analyzed consistently using atomic absorption spectrometry.

The dispersion in the analyses of samples with low silica concentrations is acceptable for both the dilution and direct injection methods. The large dispersion in the analyses of high SiO_2 samples may be due to a variety of factors including carbonization of the atomic absorption spectrometer slit, matrix-effects and the presence of colloidal silica, among others, which require further study. However, it is also apparent that recalibration of the spectrometer after one or two sample analyses is required. Four or five standards should be run in order to calibrate the spectrometer. When there is a need for recalibration after only one or two samples, it is difficult to demonstrate that the spectrometer was even working properly during the calibration.

High SiO_2 samples should always be diluted for atomic absorption analysis. However, strong dilution of samples also produces high analytical errors, since the dilution factor is directly multiplied by the instrumental error to calculate the total error in the analysis (see Table 3). In addition, there is the possibility of a systematic error in the dilution technique. This systematic error is also multiplied by the dilution factor. Together, these factors explain the higher analytical errors in the samples with high silica concentrations.

We conclude that it is urgent to conduct an interlaboratory calibration for a high range of silica concentrations that involves a larger number of laboratories in order to define the optimum dilution factor for each instrument. It should also be noted that the analytical error at high SiO_2 concentrations is not a consequence of silica deposition during storage and transportation because the commercial standards used are created taking these factors into consideration.

4. Conclusion

The analytical error for silica increases with increasing concentration as a consequence of limitations in analyzing higher concentration samples. Without dilution, there are limits to the application of atomic absorption spectrometry, whereas with dilution the high dilution factor produces large errors. However, the dilution technique is better than the direct injection of higher concentration samples. There are also systematic errors in the analytical data of Labs I and IV, analyzed by AA and CO, respectively, but the refinement of such systematic errors is easier than mitigating random instrument errors.

The interlaboratory calibration program should be continued to ensure a high level of analytical quality by the participating laboratories. Reliable analytical results are crucial for geochemical modeling of hydrothermal systems.

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