Inter-laboratory Comparison as a Tool to Improve Accuracy in the Analysis of Geothermal Waters

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ABSTRACT

Based on inter-laboratory comparison exercises sponsored by the International Atomic Energy Agency, Vienna (IAEA) in 1999, 2000, 2001 and 2003, 66.7 % of the laboratories that regularly participate in this activity have either maintained their good performance or improved their performance over the years. An increase in the number of laboratories that obtained statistically accepted results above 80% also indicates that there are improvements in the analytical performance of these laboratories.

Analytical results were evaluated using statistical tools, such as Dixon, Grubbs, Skewness and Kurtosis tests, at 95% level of confidence to identify outlying values. Reference values of each parameter analyzed were determined as consensus among expert laboratories.

Chemical parameters with high statistical outliers are Cl in low levels and HCO_3 and SiO_2 in highly saline water. Ca has consistently high statistical outliers in all inter-laboratory comparison exercises for all types of water. Na results are considered highly reproducible. By calculating the z-scores of each parameter analyzed, a long-term evaluation may be carried out by the laboratory to assess their individual performance and determine ways to improve their analytical measurements.

INTRODUCTION

Geothermal systems are characterized by the chemistry of their fluids. Considerable amount of information is derived from its chemical composition such as determining the origin, predicting deep temperature by geothermometry and monitoring changes in the reservoir due to steam utilization. Accurate chemical analysis is essential in order to correctly predict reservoir temperatures and successfully manage a geothermal resource.

The accuracy of a chemical analysis may be measured by means of proficiency testing through inter-laboratory comparison exercises. This is a tool used by many laboratories to continually monitor and improve their performance relative to each other. This activity also creates a venue for an exchange of knowledge in chemical analysis and establishes high level of measuring capability among participating laboratories (ISO/IEC 43, 1997).

Geothermal waters have high concentrations of Na, Ca, K, SiO_2, and SO_4. These components are known to interfere in most analysis and require specific procedures designed to minimize these interferences.

The IAEA has conducted inter-laboratory comparison exercises of geothermal water chemistry in 1985, 1997, 1999, 2000, 2001 and 2003 (Verma and Santoyo, 2002). This paper attempts to summarize and evaluate the results of inter-laboratory comparison conducted in 1999-2003 and demonstrate how each laboratory may use information obtained from these exercises to further improve their performance.

2. METHODOLOGY OF INTERLABORATORY COMPARISON

Inter-laboratory Comparison of Geothermal Water Chemistry in 1999, 2000, 2001 and 2003 have been jointly organized by IAEA and PNOC EDC. Geothermal water samples were collected from the Geothermal Fields of Indonesia and Thailand in 1999 and the Philippines in 2000, 2001 and 2003. The samples were prepared by filtration using 0.45 μm membrane filter and divided into two portions. One portion consisted of untreated sample and the other portion was acidified with HNO_3 until pH <2 was attained. Untreated samples were analyzed for pH, conductivity, HCO_3, Cl and SO_4 while acidified portions were analyzed for SiO_2 (total), B, F, Na, K, Ca, Mg, Li and NH_3.

Geochemistry laboratories in East Asia and Pacific, Latin American and African regions including other countries involved in geothermal development participated in these activities. Results of two trials for each parameter were reported by the laboratories, together with the mean, standard deviation, standard uncertainty and method used in analyzing various parameters. Consensus values were determined from the results of reference laboratories chosen for their expertise in geothermal water analysis. As standard practice, identities of the laboratories are not revealed and they are identified only by laboratory codes (Alvis-Isidro et al. 2001).

The analytical results were evaluated using statistical tools, AQCS (1999) and HISTO (2000-2003) programs, involving Dixon, Grubbs, Skewness and Kurtosis tests at 95% level of confidence (Radecki and Trinkl, 1999). Results that passed these statistical tests are considered good results. However, outlying results would prompt each laboratory to review their method and procedures and find ways to improve the accuracy of their analysis.

3. RESULTS OF INTERLABORATORY COMPARISON (1999-2003)

Based on the four inter-laboratory comparison exercises conducted in 1999-2003, individual performance of these laboratories show at least 66.7% have improved or maintained their good performance while the remaining 33.3% barely improved or did not improve their analytical performance (Figure 1A).
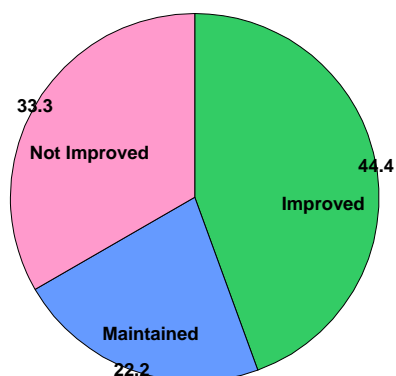
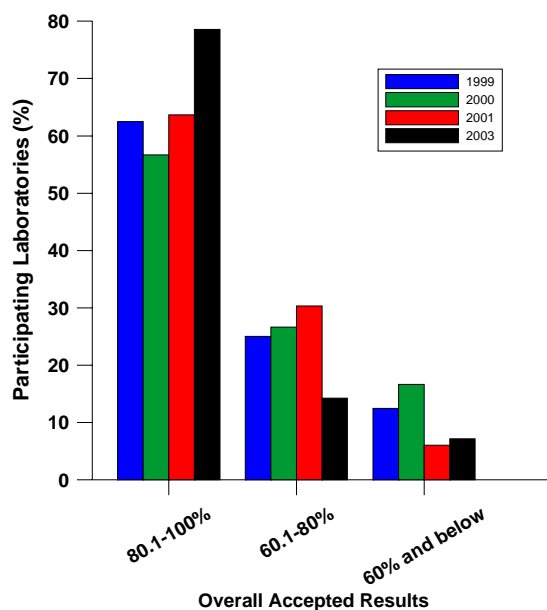**Figure 1A: Overall Performance in Interlaboratory Comparison of Geothermal Water Chemistry (1999-2003)**

Figure 1B: Classified Percent Accepted Results in Interlaboratory Comparison of Geothermal Water Chemistry (1999-2003)

There is a general increase in the number of laboratories that obtained statistically accepted results above 80%, from 62.5 % in 1999, 56.7 % in 2000, 63.6 % in 2001 and 78.6 % in 2003 (Figure 1B).

Laboratory performance may be assessed by monitoring statistically accepted results in all inter-laboratory comparison exercises. Selected laboratories were evaluated and assigned codes, namely, Ref, L1, L2, L3, L4, L5, L6 (Figure 2). Ref refers to one of the reference laboratories, L1 and L2, exemplify laboratories that have significantly improved its analytical performance from 1999 to 2003. This constitutes 44.4% of all the laboratories participating in this inter-laboratory comparison. L3 and L4 represent laboratories that have consistently maintained the quality of their analytical results, comprising 22.2% of all the laboratories. L5 and L6 are laboratories that have not improved their analytical performance as shown by the decrease in overall accepted results from 1999 to 2003. This constitutes 33.3% of all the laboratories.
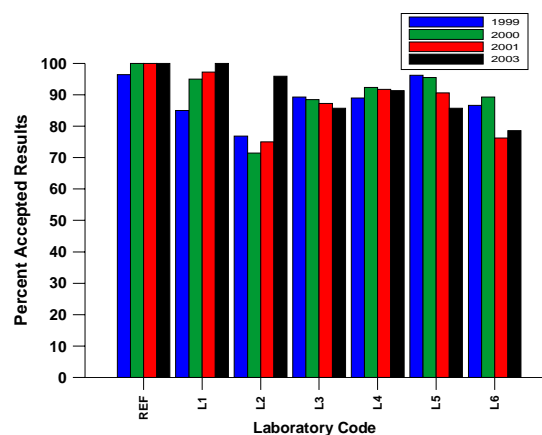

Figure 2: Overall Percent Accepted Results of Selected Laboratories in Inter-laboratory Comparison of Geothermal Water Chemistry (1999-2003)
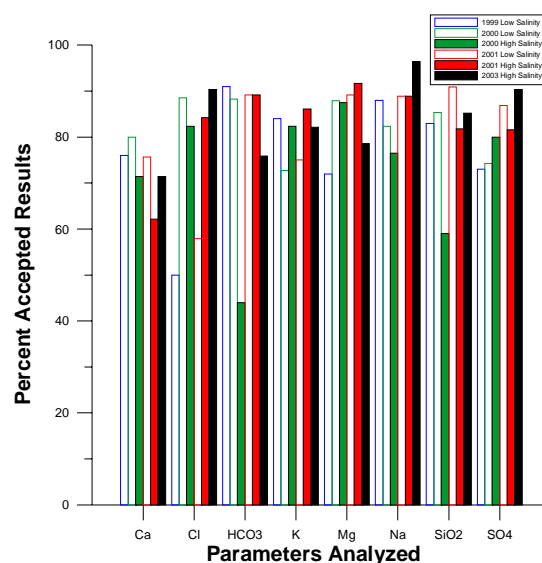

Figure 3: Percent Accepted Results for Selected Parameters (1999-2003)

The most important parameters used in geochemistry are Ca, Cl, HCO_3, K, Mg, Na, SiO_2 and SO_4. Laboratory performance in these parameters is presented in Figure 3. Low salinity samples are shown as open bars while high salinity samples are depicted as bold colored bars.

For low salinity water, significantly low percent accepted results or more outlying data were obtained in Cl analysis. A review of the method used by the different laboratories indicates that most of the outlying data were analyzed using titrimetric method. This method, also known as Mohr method, is not accurate in low chloride levels. Alternative methods are Ion Chromatography, High Performance Liquid Chromatography, Colorimetric, modified Potentiometric /Titrimetric and Ion Selective Electrode.

In highly saline water, HCO_3 and SiO_2 have low % accepted results in the 2003 inter-laboratory comparison. These chemical constituents are relatively unstable due to evolution of CO_2 gas and polymerization of SiO_2. Compared with the other parameters, Ca obtained consistently low % accepted results in all inter-laboratory comparison activities for all types of water. Presence of other chemical constituents such as Mg, SO_4 and SiO_2 are known to interfere in the analysis. The use of chemical

suppressants or releasing agents is recommended when analyzing Ca by atomic absorption spectrophotometry.

For laboratories that have participated in two or more inter-laboratory comparison activities, a z-score chart is plotted to determine the variability of its performance and detect any general trends or inconsistencies.

The z-score is calculated following the equation:

$$Z = (x - X)/\sigma$$

where x is the result, X is the assigned value and σ is the standard deviation of the inter-laboratory comparison.

Samples were classified as high, medium and low salinity and the z-scores were calculated for each type of sample. A z-score between 2.0 and 3.0 and between –2.0 and –3.0 is a "warning signal" while a z-score above 3.0 and below –3.0 is an "action signal". An "action signal" or two "warning signals" should prompt each laboratory to investigate their analytical method or procedure (ISO/IEC, 1997)

The z-score charts of the selected laboratories, Ref, L1, L2, L3, L4, L5 and L6, are presented in Figures 4A-D and 4E-H. Based on their z-scores, Cl, Ca and SiO_2 are parameters that give the highest action signals.

In Figures 4A and 4D, the z-score charts show that L3 and L5 have problems in Ca and K analyses in 2001, respectively, as revealed by z-scores greater than 3 for all samples. These results were also identified as outliers and have prompted the laboratories to correct their analytical procedures. Ca results of L3 were considered statistically acceptable in 2003 while L5 did not submit K results during the 2003 inter-laboratory comparison for some reasons. L2 and L6 also have problems in SiO_2 analysis in 2000 and 2001. Adjustments may have been done which also improved their performance in the 2003 inter-laboratory comparison (Figure 4G).

Ref, L2, L3 and L4 laboratories have action signals in low chloride samples consistent with earlier observation in Figure 3. These action signals should convince the laboratories to review their analytical method in low chloride and shift to a more sensitive method.

HCO_3, Mg and SO_4 also have z-scores greater than 3 but these have been corrected in following inter-laboratory comparison exercises. Compared with the other parameters, Na results are considered highly reproducible.

Sufficient data have been generated in these inter-laboratory comparison activities. By calculating the z-scores of each parameter analyzed, a long-term evaluation may be carried out by the laboratory to assess their individual performance and determine ways to improve their analytical measurements.

4. CONCLUSION

The general increase in the number of laboratories that obtained at least 80% percent accepted results, from 62.5 % in 1999 to 79.3 % in 2003, indicates that there are improvements in the analytical performance of laboratories that participate in this activity.

Using the z-score chart or other statistical tools, a long-term evaluation may be carried out by each laboratory to assess their individual performance and determine ways to improve their analytical measurements.

Data obtained in these inter-laboratory comparison exercises provide participating laboratories with information to help them demonstrate and improve their laboratory performance. A regular independent technical assessment also helps laboratories build confidence in generating reliable analytical results.

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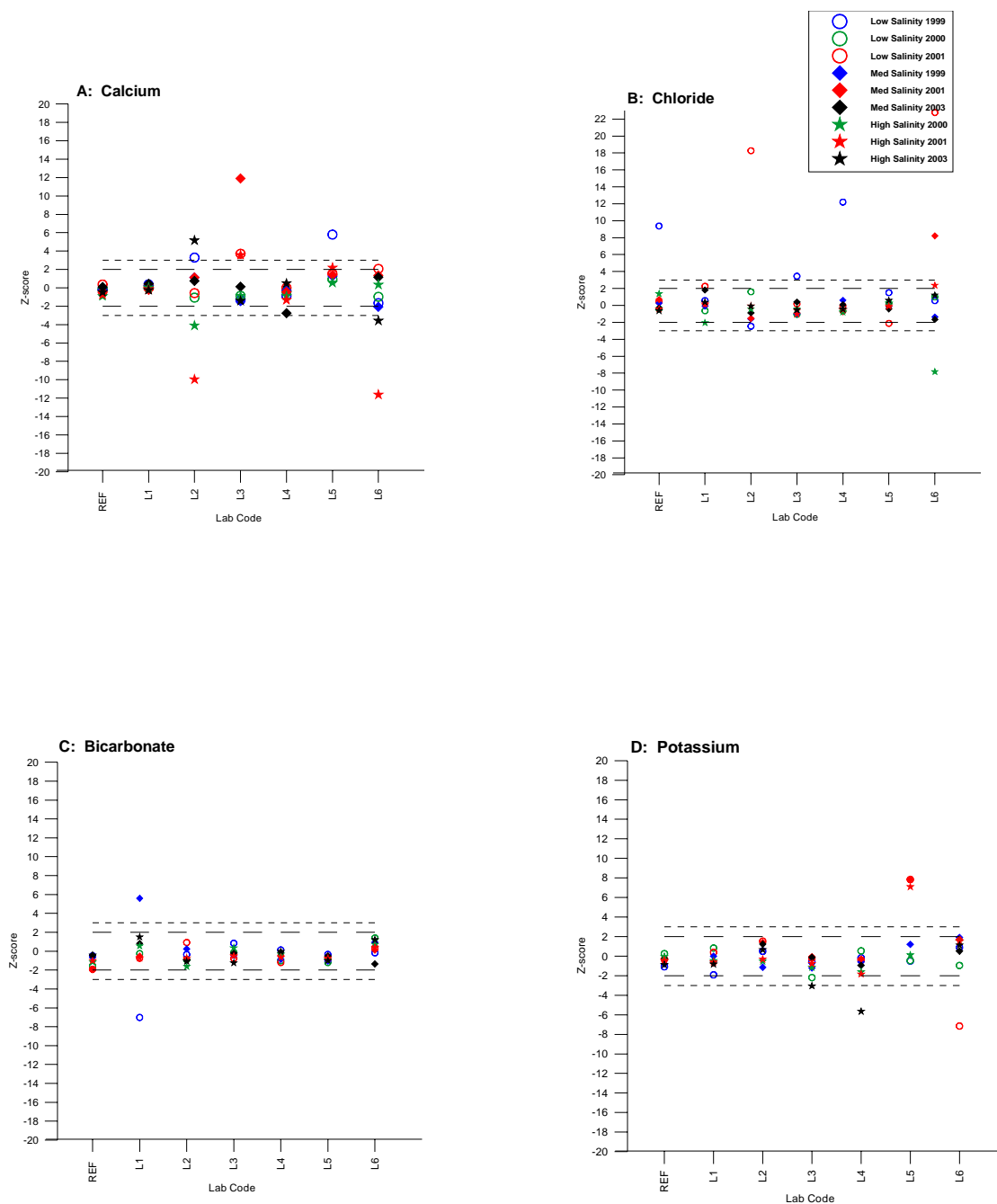
Figure 4A-D: Z-score Charts for Calcium, Chloride, Bicarbonate and Potassium of Selected Laboratories
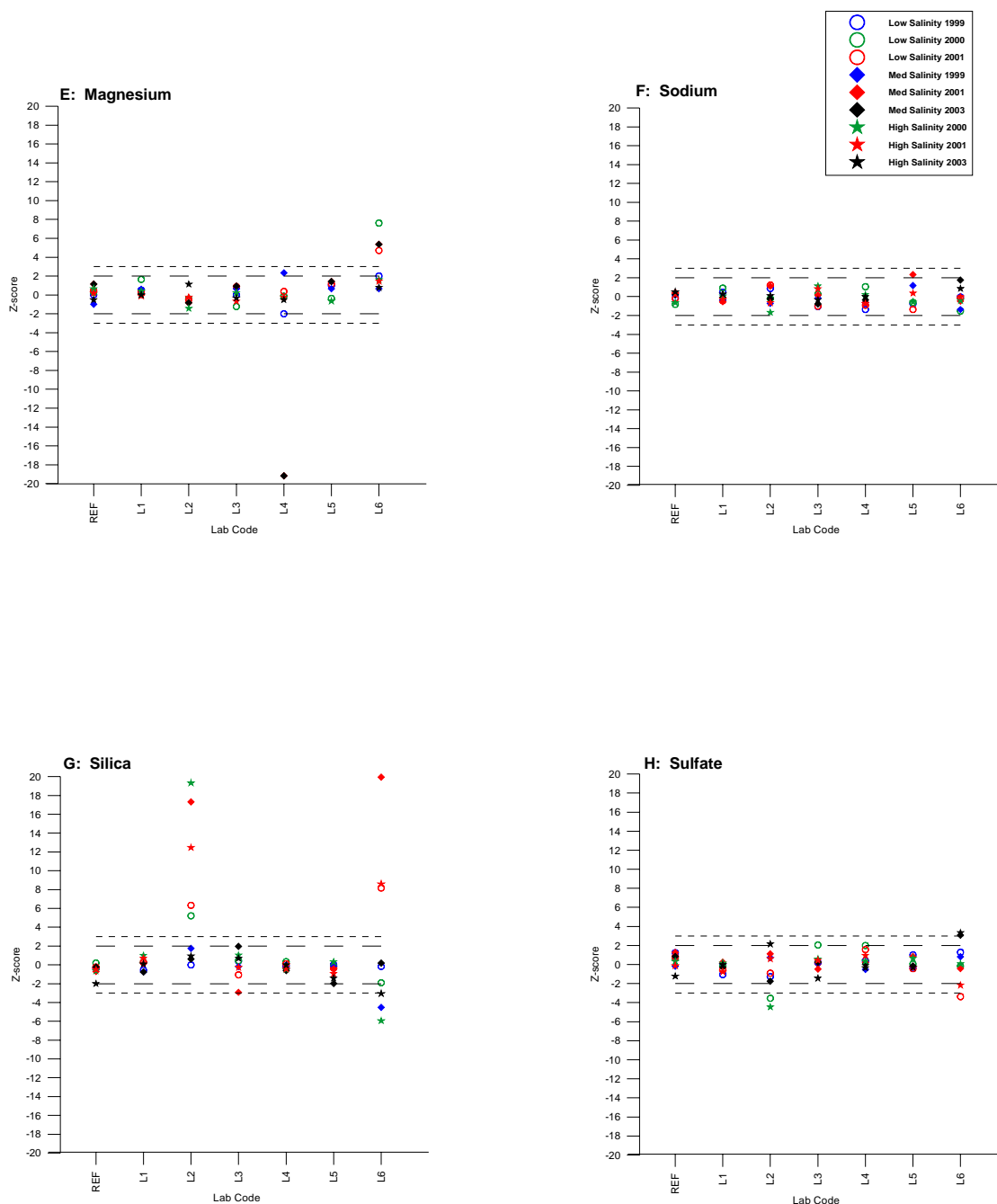
Figure 4E-H: Z-score Charts for Magnesium, Sodium, Silica and Sulfate of Selected Laboratories