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Laboratory Technique Enhancement for the Analysis of Geothermal Fluids in EDC Geothermal Fields and Its Impact to the Overall Efficiency of the Laboratory Analytical Processes

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ABSTRACT

This study aims to improve the current analytical procedures of EDC laboratories in terms of sample volume requirement, analysis speed, waste generation and environmental impact to improve the overall productivity of its analytical processes. Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES) an analytical technique generally used for the analyses of metals with an advantage of improved analysis speed and reduce analytical volume requirement is the method proposed to succeed the current methods used in the analysis of Boron (Titration and UV-Vis Spectroscopy) , SiO_2 (UV-vis spectroscopy), and metals (AAS). Current procedures used for Boron, Silica and metal analyses are time consuming, with longer chemical exposure due to extended sample preparation time and high chemical waste producer. In this study, several verification studies to ensure the applicability of ICP-OES in geothermal brine matrix and comparative studies between ICP-OES and current methods to assess the degree of agreement of the methods were conducted. The results of the verification studies showed that ICP-OES is a good technique for the analysis of metals, Silica and Boron in terms of linear dynamic range, detection limits, accuracy and percent recovery in both low and high saline geothermal fluids. Moreover, proficiency test result showed that the result provided by the new method is precise when compared to the results of other laboratory and accurate as shown by the high recovery percentage.

With the positive results in the verification and proficiency testing, the transition to adopt ICP-OES as a new method for EDC laboratories yielded several benefits. The method reduced the volume requirement for B, SiO_2 and metals (Na, K, Ca, Mg, Fe, Mn, Rb, Li, Al) analyses down to 100mL from 700mL (~86% reduction), analysis time by 88% and analytical cost to 70%. Volume reduction significantly lessened the effort in terms of handling and mobilization during sampling, shipping and logistics costs, the amount of waste generated by the laboratory, the chemical exposure of the analyst due to the new method, and heightened laboratory productivity as shown in the decrease in sample preparation and analysis time. Still, this volume requirement is limited only to the above-mentioned parameters; additional volume would be required for a complete suite analysis of geothermal samples.

1. INTRODUCTION

Recent advances in analytical techniques allow the modification of established analytical procedures to improve the quality of results, analysis speed; minimize waste generation and environmental impact. High volume requirement of an analyses due to outdated methods, however analytically sound, translate to high waste generation and analytical cost. In addition, analysis time and cost per analysis is highly dependent on the method used, outdated methods usually require longer analytical time and high analytical cost. Atomic Absorption Spectroscopy (AAS) is one of the established methods used for the analysis of metals (Na, K, Ca, Mg, Fe, Mn, Rb, Li, Al) currently adopted by the laboratory. This method is based on the absorption of radiation by their free atoms to quantify the amount of the element of interest. It is a sequential analytical technique wherein analysis is done one element at a time making it laborious if multiple elements are needed to be analyzed. UV-vis spectroscopy on the other hand is used for the analysis of Silica (SiO_2) and samples with low Boron (B) concentrations (e.g. molybdosilicate method for high SiO_2, heteropoly-blue method for low SiO_2, Azomethine-H complexation for low B). This method is based on the absorption of ultraviolet and visible radiation by electrons in the molecules of an absorbing sample. The intensity of absorption translates to the concentration level of the chromophore of interest. Potentiometric titration whilst the addition of mannitol is used for the analysis of boron at high concentrations (i.e 1.00 mg L^{-1} to 250 mg L^{-1}). These are highly time consuming methods since intensive sample preparation requiring several chemicals are needed to convert the SiO_2 and B into a detectable species. To address these issues, Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES) is considered to substitute the current analytical procedures of the laboratory.

ICP-OES is a powerful technique in determining trace levels of metals in a variety of sample matrices, the technique uses the emission spectra of the sample to determine and quantify the elements present. Liquid samples are introduced into the plasma through a sample introduction system that converts liquid to aerosols. In the plasma, sample desolvation, ionization, excitation and emission happen. Emission lines produced by the sample will identify the elements present and will be quantified based on the intensity of the emission lines. ICP-OES technique has high sample throughput enabling analysis of large volume of samples, simultaneous analysis of multiple elements in a sample will greatly decrease the sample analysis time and the high-temperature plasma (~10,000K) eliminates chemical interferences and most of the interferences associated with the sample matrix. With this technical improvements, laboratories like Intertek, SGS, GNS and Thermochem have already adopted ICP-OES as a method for the analysis of metals.

This study aims to improve the current analytical procedures of EDC laboratories in terms of sample volume requirement, analysis cost and speed, waste generation and environmental impact to improve the overall productivity of its analytical processes. As a ISO:IEC 17025 accredited laboratory, method verification, interlaboratory comparison is conducted to assess the applicability of the method while time and motion, cost analysis and volume reduction studies will be used to evaluate the impact of this method transition to the laboratory's analytical processes.

2. METHODOLOGY

2.1 Method verification

Acidified water samples were used for this study. Prior to analysis, water samples were filtered and diluted with HNO_3 acid to adjust the concentration of the analyte to a level suitable for detection limit test and spike recovery evaluation. Determination of linear dynamic range (LDR); estimation of instrument detection limit (IDL); and determination of method detection limit (MDL), reliable detection limit (RDL), limit of quantitation (LOQ), accuracy and precision were the performance characteristics used for the verification process. MDL is the measured concentration at which there is a 95 or 99% probability that an analyte is present while LOQ is the lowest amount of analyte which can be quantitatively determined with precision and accuracy appropriate to analyte and matrix considered.

2.2 Proficiency testing

Proficiency testing, a quality assurance program of EDC chemistry laboratories was conducted to evaluate the effectiveness of the analytical method verified. Synthetic water samples were prepared using NIST traceable standards and were distributed to all participating laboratories. Precision and accuracy of test results were evaluated for this activity. Precision was evaluated based on z-scores wherein values within ± 2 were considered acceptable. Accuracy was evaluated based on percent recovery against theoretical value.

2.3 Time and motion analysis, analytical cost comparison and volume reduction evaluation

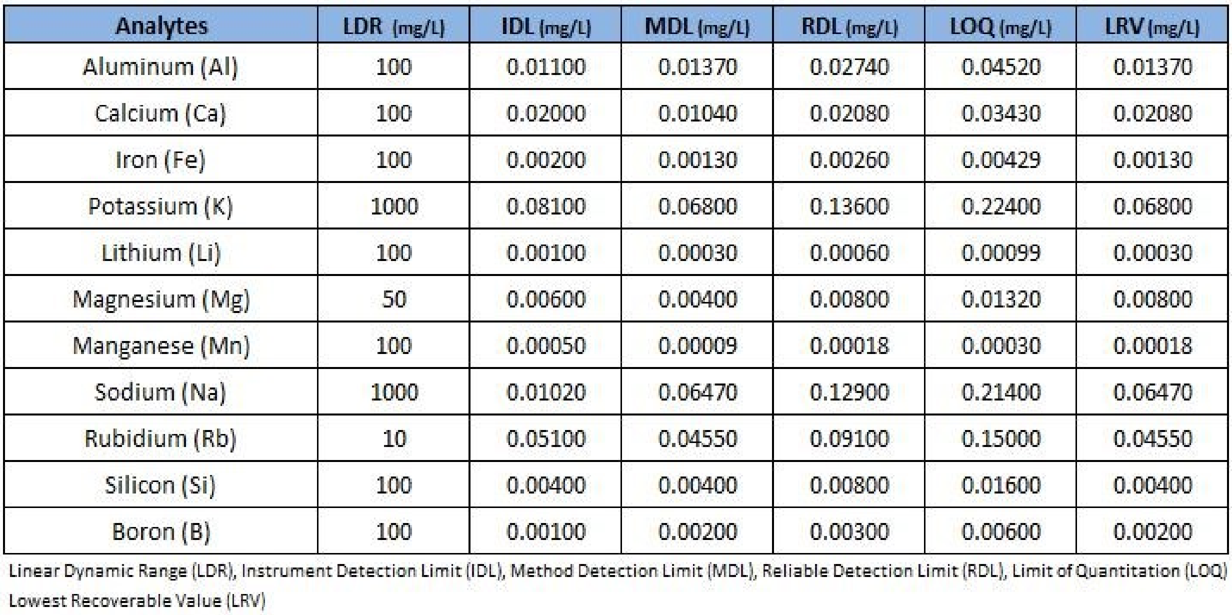
To assess the impact of the ICP-OES method, analysis time, analytical cost and volume requirement for the analyses were evaluated.

3. RESULTS AND DISCUSSION

3.1 Method verification

Filtered acidified geothermal brine samples were analyzed in a span of 1 month to establish the required performance characteristics to elicit the applicability of ICP-OES method in the analysis of geothermal brine. Linear dynamic range, a measure of proportionality of a signal to concentration in a linear fit model, established for all analytes of interest are wider compared to that determined using the conventional method (Tables 1, 2). This improvement in the linear dynamic range reduces the uncertainty during the analysis due to sample dilution. For the instrument detection limit, values were obtained by analyzing eight (8) replicates of blank solutions in three trials for a span of 1 week. This was conducted to determine the lowest concentration distinguishable from zero. Calculated standard deviation from the readings was multiplied by 3 to estimate the IDL (Figure 1). Estimated IDL values were then used to calculate the MDL, RDL and LOQ values per analyte (Table 1). Calculated detection limits were then tested for recovery. This was done to establish the lowest recoverable values (LCV) with an acceptable degree of accuracy and precision. Comparing the LCVs established using ICP-OES to that of the current methods showed a huge improvement, ICP-OES results were of much lower concentrations This increases the reliability of results when analyzing samples with very low analyte concentrations. Accuracy and precision analysis results also showed that even with the decrease in the detection limits the equipment is capable of analyzing these concentrations to an acceptable recovery and RSD values. Results from these performance characteristics verified the applicability of ICP-OES method for the analysis of metals, SiO_2 (as Si) and B in geothermal brine.

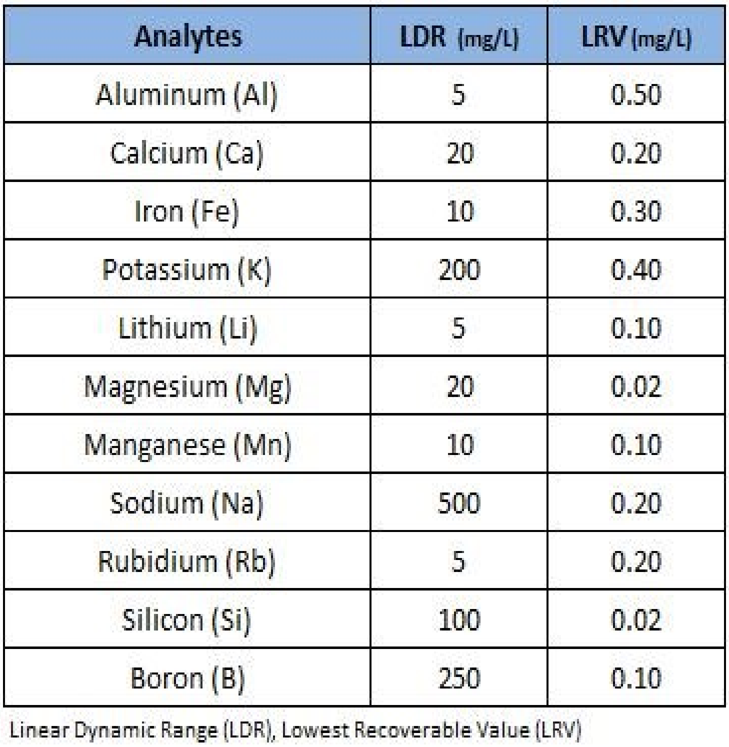
Table 1: ICP-OES method verification results



Analytes	LDR (mg/L)	IDL (mg/L)	MDL (mg/L)	RDL (mg/L)	LOQ (mg/L)	LRV (mg/L)
Aluminum (Al)	100	0.01100	0.01370	0.02740	0.04520	0.01370
Calcium (Ca)	100	0.02000	0.01040	0.02080	0.03430	0.02080
Iron (Fe)	100	0.00200	0.00130	0.00260	0.00429	0.00130
Potassium (K)	1000	0.08100	0.06800	0.13600	0.22400	0.06800
Lithium (Li)	100	0.00100	0.00030	0.00060	0.00099	0.00030
Magnesium (Mg)	50	0.00600	0.00400	0.00800	0.01320	0.00800
Manganese (Mn)	100	0.00050	0.00009	0.00018	0.00030	0.00018
Sodium (Na)	1000	0.01020	0.06470	0.12900	0.21400	0.06470
Rubidium (Rb)	10	0.05100	0.04550	0.09100	0.15000	0.04550
Silicon (Si)	100	0.00400	0.00400	0.00800	0.01600	0.00400
Boron (B)	100	0.00100	0.00200	0.00300	0.00600	0.00200

Linear Dynamic Range (LDR), Instrument Detection Limit (IDL), Method Detection Limit (MDL), Reliable Detection Limit (RDL), Limit of Quantitation (LOQ) Lowest Recoverable Value (LRV)

Table 2: Established LDR and LRV using the conventional methods



Analytes	LDR (mg/L)	LRV (mg/L)
Aluminum (Al)	5	0.50
Calcium (Ca)	20	0.20
Iron (Fe)	10	0.30
Potassium (K)	200	0.40
Lithium (Li)	5	0.10
Magnesium (Mg)	20	0.02
Manganese (Mn)	10	0.10
Sodium (Na)	500	0.20
Rubidium (Rb)	5	0.20
Silicon (Si)	100	0.02
Boron (B)	250	0.10

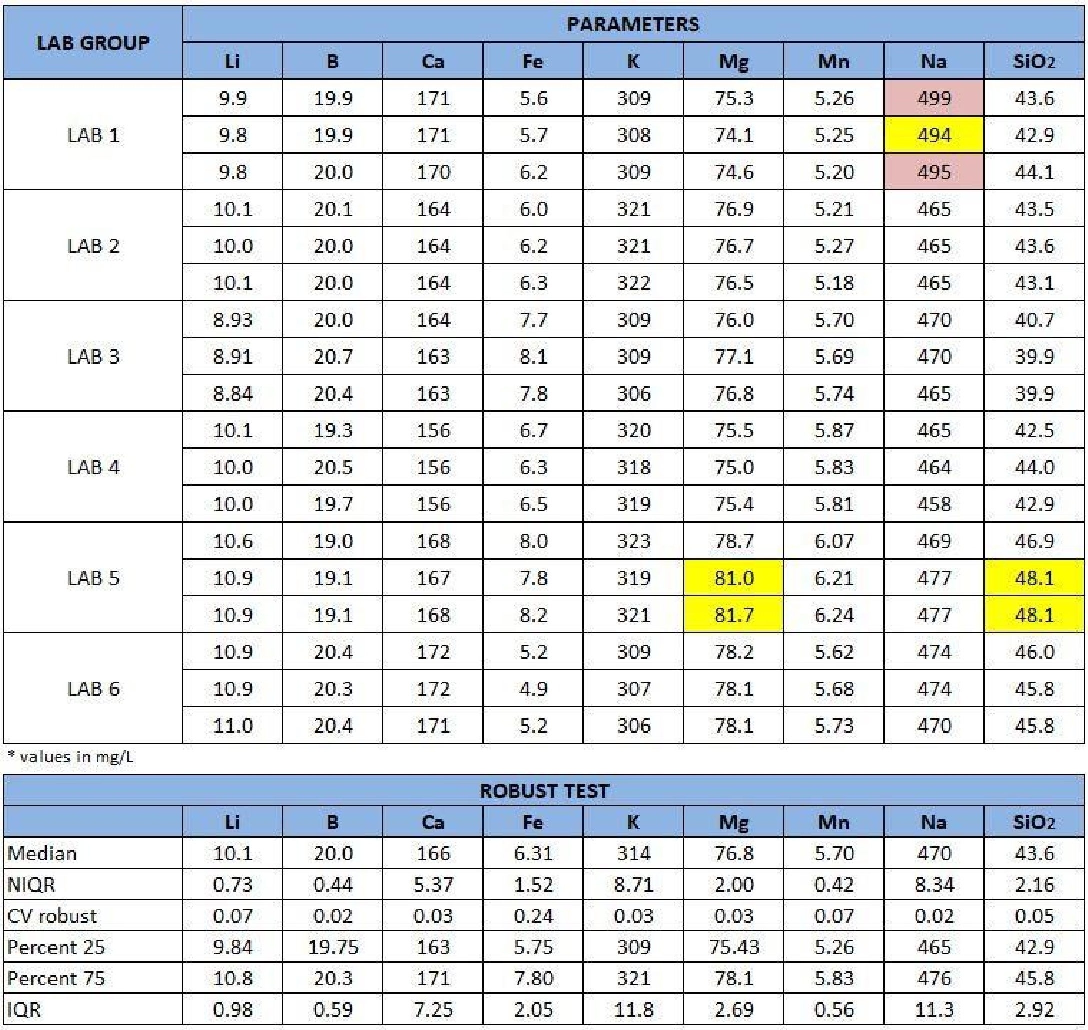
Linear Dynamic Range (LDR), Lowest Recoverable Value (LRV)

3.2 Proficiency testing

A total of six laboratories participated in the proficiency testing and were coded as Lab 1, Lab 2, up to Lab 6, with Lab 2 as the laboratory of interest. Precision results were evaluated based on robust z-scores using median and normalized interquartile ranges. Cells in yellow boxes are questionable data or in the warning range (z-score range of ±2 to ±3) while values in pink cells are outliers in z-score test however results were considered acceptable once reported uncertainty was incorporated. As shown in Table 3, all results submitted by Lab 2 were precise based on the result of z-score test, a precision relative to the result of other participating laboratories. ICP-OES results provided by Lab 2 are not significantly different to that of the other laboratories using the conventional methods (Lab 4, 5 and 6).

In addition, accuracy test showed that the ICP-OES method of Lab 2 is accurate with recovery range from 90%-105% (Table 4) for all analyte of interest. Results in the proficiency test provide concrete evidence on the applicability of ICP-OES method in the analysis of metals, SiO_2 and B.

Table 3: Summary of analytical results with robust test evaluation

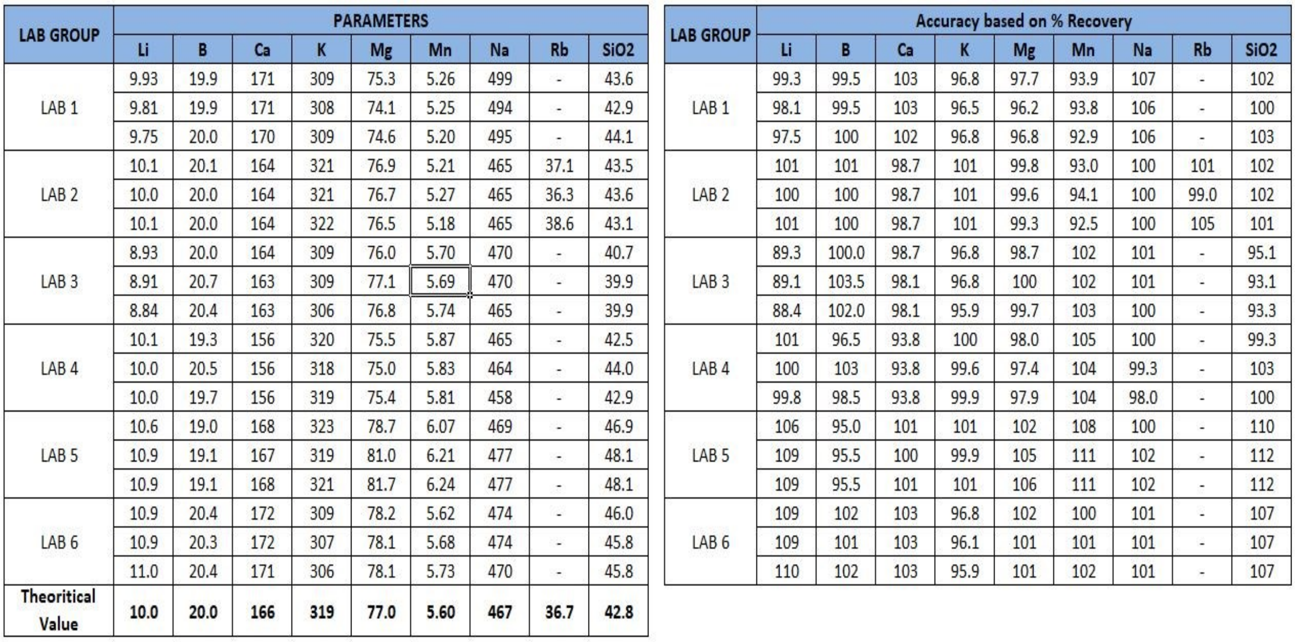


LAB GROUP	PARAMETERS								
	Li	B	Ca	Fe	K	Mg	Mn	Na	SiO_2
LAB 1	9.9	19.9	171	5.6	309	75.3	5.26	499	43.6
	9.8	19.9	171	5.7	308	74.1	5.25	494	42.9
	9.8	20.0	170	6.2	309	74.6	5.20	495	44.1
LAB 2	10.1	20.1	164	6.0	321	76.9	5.21	465	43.5
	10.0	20.0	164	6.2	321	76.7	5.27	465	43.6
	10.1	20.0	164	6.3	322	76.5	5.18	465	43.1
LAB 3	8.93	20.0	164	7.7	309	76.0	5.70	470	40.7
	8.91	20.7	163	8.1	309	77.1	5.69	470	39.9
	8.84	20.4	163	7.8	306	76.8	5.74	465	39.9
LAB 4	10.1	19.3	156	6.7	320	75.5	5.87	465	42.5
	10.0	20.5	156	6.3	318	75.0	5.83	464	44.0
	10.0	19.7	156	6.5	319	75.4	5.81	458	42.9
LAB 5	10.6	19.0	168	8.0	323	78.7	6.07	469	46.9
	10.9	19.1	167	7.8	319	81.0	6.21	477	48.1
	10.9	19.1	168	8.2	321	81.7	6.24	477	48.1
LAB 6	10.9	20.4	172	5.2	309	78.2	5.62	474	46.0
	10.9	20.3	172	4.9	307	78.1	5.68	474	45.8
	11.0	20.4	171	5.2	306	78.1	5.73	470	45.8

* values in mg/L

ROBUST TEST									
	Li	B	Ca	Fe	K	Mg	Mn	Na	SiO_2
Median	10.1	20.0	166	6.31	314	76.8	5.70	470	43.6
NIQR	0.73	0.44	5.37	1.52	8.71	2.00	0.42	8.34	2.16
CV robust	0.07	0.02	0.03	0.24	0.03	0.03	0.07	0.02	0.05
Percent 25	9.84	19.75	163	5.75	309	75.43	5.26	465	42.9
Percent 75	10.8	20.3	171	7.80	321	78.1	5.83	476	45.8
IQR	0.98	0.59	7.25	2.05	11.8	2.69	0.56	11.3	2.92

Table 4: Accuracy test results



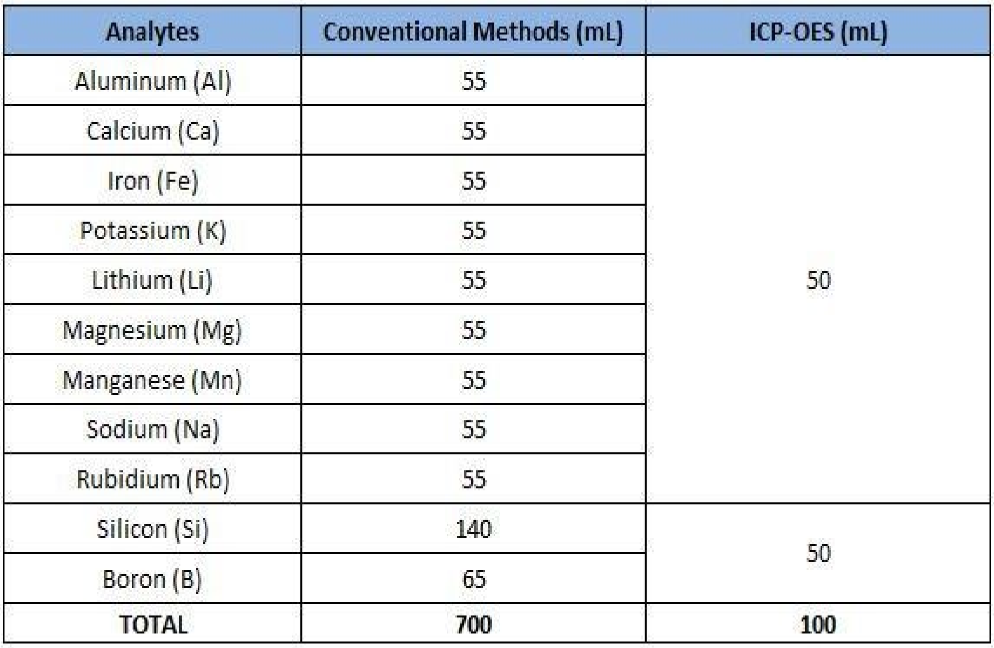
LAB GROUP	PARAMETERS								
	Li	B	Ca	K	Mg	Mn	Na	Rb	SiO2
LAB 1	9.93	19.9	171	309	75.3	5.26	499	-	43.6
	9.81	19.9	171	308	74.1	5.25	494	-	42.9
	9.75	20.0	170	309	74.6	5.20	495	-	44.1
LAB 2	10.1	20.1	164	321	76.9	5.21	465	37.1	43.5
	10.0	20.0	164	321	76.7	5.27	465	36.3	43.6
	10.1	20.0	164	322	76.5	5.18	465	38.6	43.1
LAB 3	8.93	20.0	164	309	76.0	5.70	470	-	40.7
	8.91	20.7	163	309	77.1	5.69	470	-	39.9
	8.84	20.4	163	306	76.8	5.74	465	-	39.9
LAB 4	10.1	19.3	156	320	75.5	5.87	465	-	42.5
	10.0	20.5	156	318	75.0	5.83	464	-	44.0
	10.0	19.7	156	319	75.4	5.81	458	-	42.9
LAB 5	10.6	19.0	168	323	78.7	6.07	469	-	46.9
	10.9	19.1	167	319	81.0	6.21	477	-	48.1
	10.9	19.1	168	321	81.7	6.24	477	-	48.1
LAB 6	10.9	20.4	172	309	78.2	5.62	474	-	46.0
	10.9	20.3	172	307	78.1	5.68	474	-	45.8
	11.0	20.4	171	306	78.1	5.73	470	-	45.8
Theoritical Value	**10.0**	**20.0**	**166**	**319**	**77.0**	**5.60**	**467**	**36.7**	**42.8**

LAB GROUP	Accuracy based on % Recovery								
	Li	B	Ca	K	Mg	Mn	Na	Rb	SiO2
LAB 1	99.3	99.5	103	96.8	97.7	93.9	107	-	102
	98.1	99.5	103	96.5	96.2	93.8	106	-	100
	97.5	100	102	96.8	96.8	92.9	106	-	103
LAB 2	101	101	98.7	101	99.8	93.0	100	101	102
	100	100	98.7	101	99.6	94.1	100	99.0	102
	101	100	98.7	101	99.3	92.5	100	105	101
LAB 3	89.3	100.0	98.7	96.8	98.7	102	101	-	95.1
	89.1	103.5	98.1	96.8	100	102	101	-	93.1
	88.4	102.0	98.1	95.9	99.7	103	100	-	93.3
LAB 4	101	96.5	93.8	100	98.0	105	100	-	99.3
	100	103	93.8	99.6	97.4	104	99.3	-	103
	99.8	98.5	93.8	99.9	97.9	104	98.0	-	100
LAB 5	106	95.0	101	101	102	108	100	-	110
	109	95.5	100	99.9	105	111	102	-	112
	109	95.5	101	101	106	111	102	-	112
LAB 6	109	102	103	96.8	102	100	101	-	107
	109	101	103	96.1	101	101	101	-	107
	110	102	103	95.9	101	102	101	-	107

3.3 Time and motion analysis, analytical cost comparison and volume reduction evaluation

Evaluation of these parameters provides conclusive data on the positive effect on the transition to using ICP-OES over the current laboratory methods. Time and motion analysis presented a drastic decrease in the time required for the analytes of interest to be analyzed. Data showed that a significant decrease of about 88% analysis time was observed when ICP-OES method was used instead of the current laboratory methods. For analytical charges, computation was based on direct material costs, labor costs and overhead costs per analysis. Direct material costs include chemicals, standard reagents, gas and acid requirements; equipment, utilities and indirect material costs were considered in the overhead costs. Evaluation showed that 70% of the analytical cost was reduced when ICP-OES was used. With an annual average of 1,000 liquid samples that the laboratory receives, a substantial amount of saving is projected. This is under the assumption that all samples will be analyzed for all the parameters mentioned. In the case of volume reduction study, it showed an ~86% decrease in the requirement, from 700mL to 100mL (Table 5).Calculation was made based on the actual consumption per analysis, allowance was also considered in determining the final volume requirement for quality assurance requirement (e. g. spike recovery, duplicates) and possible reanalysis. This volume reduction in turn reduces the amount of waste generated by the laboratory making it more environment friendly, lessened the effort in terms of handling and mobilization during sampling, shipping and logistics cost.

Table 5: Comparison of the volume requirements of the conventional methods vs that of the ICP-OES



Analytes	Conventional Methods (mL)	ICP-OES (mL)
Aluminum (Al)	55	50
Calcium (Ca)	55	
Iron (Fe)	55	
Potassium (K)	55	
Lithium (Li)	55	
Magnesium (Mg)	55	
Manganese (Mn)	55	
Sodium (Na)	55	
Rubidium (Rb)	55	
Silicon (Si)	140	50
Boron (B)	65	
TOTAL	**700**	**100**

4. CONCLUSION

The result of the study showed that the transition from conventional analytical method in the analysis of metals, SiO_2 and Boron is beneficial to the overall efficiency of the laboratory. Method verification studies and proficiency testing results provide a concrete evidence of the applicability of ICP-OES as a new method for the laboratory. Time and motion analysis, analytical cost comparison and volume reduction evaluation on one hand lay down the benefits of the transition. 88% decrease in analysis time, 70% for the cost of analysis and 86% in volume requirement. In addition, these improvements also directly affect the laboratory's customers. Decrease in analysis time translates to shorter turn-around time of result submission and reduction in volume requirement lowers the cost during sampling, shipping and other logistical expenses.

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