STATISTICAL EVALUATION OF SOME ANALYTICAL METHODS IN THE HYDROGEO CHEMISTRY LABORATORY OF GENERAL DIRECTORATE OF MINERAL RESEARCH AND EXPLORATION

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ABSTRACT. — Several analytical methods are being employed related to various research projects and routine works on water samples in hydrogeochemistry laboratory of General Directorate of Mineral Research and Exploration. Some statistical evaluations are necessary in order to obtain accurate results for the projects related. In order to control the precision and accuracy of the chemical determinations in our laboratory, standard water samples have been requested from EPA (Environmental Protection Agency, USA). The samples donated by EPA have been analyzed for 28 species using our standard methods. Results of the determinations were compared with the true values supplied by EPA using «Studend's t test». R values have been used to investigate the presence of systematic errors at 95 % an 99 % confidence levels. Accuracy and precision of the analytical methods used have been statistically determined. No systematic error was observed for 43 results of the total of 54. Evaluation for systematic error could not be realized for 11 results. Relative percent errors were found to be in the ranges at 0-10, 11-20, 21-50 and more than 50 for 33, 10, 6,5 results respectively. As a result of this study, by applying the statistical tests for accuracy and precision, it has been determined that accurate results are obtained in most of the methods, only two methods require further development.

INTRODUCTION

A good analyst continually tempers his confidence with doubt. In an analytical laboratory in order to have a high confidence for the results, some precautions must be taken. These precautions are occasional comparisons of analytical results obtained for samples using different methods, analyzing reference samples, making replicate runs for the same samples, participating in interlaboratory and intra-laboratory studies for analytical accuracy. However, it is not possible to obtain reference samples for water quality analyses as the composition of water samples is not stable. The duties involved at the hydrogeochemistry laboratory of General Directorate of Mineral Research and Exploration are mainly water analyses related to various projects carried out in our institute. Recently, we have been dealing with water pollution control. In addition, to these duties, we are analyzing water soluble constitutes of various salts.

As we all know, water is one of the most important components of the human environment and its purity should be controlled very carefully. Consequently, accuracy and precision of the analytical methods used in all the fields mentioned above must be frequently tested using statistical methods. For this purpose, a typical study will be presented here.

METHODS

In order to control the precision and accuracy of chemical determinations in our laboratory, standard water samples have been requested from EPA Environmental Protection Agency, USA, and analyzed in our laboratory without having the knowledge of the true values. The true values were provided from EPA subsequent to completion of analyses and compared to our results. The analytical methods used for the chemical determinations are listed in Table 1.

Table 1 - Methods and instrumentation employed for results of EPA samples

Determined species or property	*Analytical method*	*Instrumentation*
pH	Potentiometry	pH meter (Corning
Specific Conductivite	conductivimetry	Conductivimeter (YSI Model 31)
Ca, Mg	EDTA titration	
Na, K	Flame emission Photometry	Flame Photometer (Eppendorf)
Cl	Ag NO_3 titration	
F	Alizarin compexon-Photometric	Spectrophotometer (Spectronic 20)
SO_4	Gravimetric	
NO_3	Brucin-Photometric	Spectrophotometer (Spectronic 20)
NH_4	Nesslerization-Photometric	Spectrophotometer (Spectronic 20)
Ortho phosphate	Ascorbic acid reduction-Photometric	Spectrophotometer (Spectronic 20)
Total phosphate	Ascorbic acid reduction-Photometric	Spectrophotometer (Spectronic 20)
As	Silver diethyl dithio-carbomate Photometric	Spectrophotometer (Spectronic 20)
Mn	Ammonium persulfate-Photometric	Spectrophotometer (Spectronic 20)
Cu, Cd, Co, Ni, Pb, Zn	Extraction-Atomic absorption	A.A.spectrophotometer (Perkin Elmer 303)
V	Catalytic oxidation-Photometric	Spectrophotometer (Coleman model 6A)
Hg	Cold vapour oxidation absorption	Photometer (Coleman 50 A)
Fe	Dipyridyl photometric	Spektrophotometer (Spectronic 20)

The samples EPA 1 (1,2) contain major element in two different concentrations; EPA 3 (1,2) fluoride and nitrate in two different concentrations; EPA 4 (1,2) ammonium, nitrate and orthophosphate in two different concentrations; EPA 5(1,2), total phosphate in two differen concentrations; EPA (1,2,3) heavy mefals in three different concentrations.

The results of chemical determinations, and number of analyses are presented in Table 2, where statistical evaluations are given in Table 3.

The terms used in Table 3 are defined as follows:

Mean value: The arithmetic mean of the different runs.

Standard deviation: For n replicate analytical results, x_1, x2, x_3,,,, x_n the sample standard deviation is calculated from the equation:

$$s = \sqrt{\frac{\Sigma i (x_i - \bar{x})^2}{n - 1}}$$

Where s = The standard deviation

$\bar{x}$ = The arithmetic mean of the results

n = The number of replicate results

$$\text{r.s.d} = \frac{s}{\bar{x}} 100$$

r.s.d = Relative standard deviation.

If r.s.d is greater than 10, the reproducibility of the method should require improvement.

Table 2 - The results of chemical determinations

Analyte	*Run 1*	*Run 2*	*Run 3*	*Run 4*	*Run 5*	*True value*
EPA 1 (1-2)						
pH (1)	8.35	8.33	8.20	—	—	8.60
pH (2)	7.40	7.60	8.05	—	—	7.70
Sp. conductivity (1) µmho/cm	500.00	500.00	480.00	—	—	572.00
Sp. conductivity (2) µmho/cm	102.00	105.00	105.00	—	—	113.00
Tot. dissolved solids (1) mg/l (180°C)	472.00	502.00	438.00	—	—	338.00
Tot. dissolved solids (2) mg/l ((180°C)	88.00	—	—	—	—	54.00
Tot. hardness (1) mg/l $CaCO_3$	140.00	160.00	135.00	—	—	135.00
Tot. hardness (2) mg/l $CaCO_3$	25.20	—	—	—	—	20.70
Ca (1) mg/l	41.20	41.60	40.50	—	—	40.60
Ca (2) mg/l	5.60	—	—	—	—	5.30
Mg (1) mg/l	10.30	—	—	—	—	8.40
Mg (2) mg/l	2.70	—	—	—	—	1.80
Na (1) mg/l	46.40	48.00	44.40	—	—	46.60
Na (2) mg/l	8.30	8.60	8.40	—	—	8.20
K (1) mg/l	9.40	9.50	8.90	—	—	9.80
K (2) mg/l	1.82	1.81	1.80	—	—	2.10
Tot. alkalinity (1) mg/l $CaCO_3$	74.40	—	—	—	—	74.70
Tot. alkalinity (2) mg/l $CaCO_3$	25.00	25.00	26.00	—	—	21.70
Cl (1) mg/l	97.20	—	—	—	—	87.90
Cl (2) mg/l	21.34	21.34	—	—	—	18.40
F (1) mg/l	1.12	1.18	1.20	—	—	1.30
F (2) mg/l	0.39	0.34	0.37	—	—	0.43
SO_4 (1) mg/l	95.00	—	—	—	—	93.60
SO_4 (2) mg/l	4.00	3.80	—	—	—	7.20
EPA 3 (1-2)						
F (1) mg/l	0.26	0.34	0.30	0.36	0.30	0.36
F (2) mg/l	2.10	2.20	2.20	2.20	2.20	2.30
NO_3 (1) mg/l N	0.22	0.45	0.68	0.34	0.25	0.22
NO_3 (2) mg/l N	9.60	10.05	—	—	—	10.10
EPA 4 (1-2)						
NH_4 (2) mg/l N	1.30	1.30	1.30	1.20	1.24	1.30
NH_4 (1) mg/l N	0.20	0.20	0.24	0.13	0.22	0.19
NO_3 (1) mg/l N	0.39	0.25	0.27	0.25	—	0.31
NO_3 (2) mg/l N	1.67	2.30	1.60	1.53	1.65	1.59
Ortho phosphate (1) mg/l P	0.03	0.03	0.03	0.02	0.03	0.03
Ortho phosphate (2) mg/l P	0.17	0.16	0.12	0.14	0.12	0.15
EPA 5 (1-2)						
Total P (1) mg/l P	0.14	0.16	0.14	0.14	—	0.14
Total P (2) mg/l P	1.07	0.99	0.69	0.73	—	0.93

Table 2 (continued)

Analyte µg/l	*Run 1*	*Run 2*	*Run 3*	*True value*
EPA Heavy metals (1,2,3)				
As (1)	60.00	—	—	24.00
As (2)	400.00	—	—	182.00
As (3)	176.00	—	—	61.00
Cd (1)	8.00	6.50	10.00	6.50
Cd (2)	90.00	55.00	110.00	59.00
Cd (3)	28.00	32.00	28.00	27.00
Co (1)	26.00	35.00	25.00	30.00
Co (2)	350.00	350.00	320.00	348.00
Co (3)	95.00	97.00	75.00	96.00
Cu (1)	10.50	14.00	8.00	8.70
Cu (2)	391.00	400.00	400.00	374.00
Cu (3)	43.00	39.00	44.00	37.00
Fe (2)	840.00	800.00	800.00	796.00
Hg (1)	0.80	0.40	1.85	0.40
Hg (2)	6.45	7.20	7.45	7.60
Hg (3)	3.65	4.50	5.50	4.40
Mn (2)	460.00	470.00	400.00	478.00
Ni (1)	75.00	32.00	25.00	8.70
Ni (2)	140.00	190.00	200.00	165.00
Ni (3)	60.00	85.00	23.00	96.00
Pb (1)	32.50	28.00	33.00	30.00
Pb (2)	325.00	400.00	330.00	383.00
Pb (3)	110.00	125.00	98.00	113.00
V (1)	71.00	56.00	—	78.00
V (2)	640.00	700.00	—	848.00
V (3)	313.00	430.00	—	470.00
Zn (1)	31.00	27.00	30.50	6.10
Zn (2)	500.00	490.00	420.00	478.00
Zn (3)	27.00	55.00	40.00	26.00

Table 3 - Statistical evaluation of chemical determinations

Analyte	*True value*	*Mean value*	*Standard deviation*	*R. stand. dev.*	t_c	*Confidence levels* % 99 *R*	% 95 *R*	*Percent error* (%)
EPA 1 (1-2)								
pH (1)	8.60	8.29	0.08	0.98	6.52	0.66	1.52	- 3.57
pH (2)	7.70	7.68	0.33	4.33	0.09	0.01	0.02	- 0.22
Sp.conductivity (1) µmho/cm	572.00	493.33	11.55	2.34	11.80	1.19	2.74	- 13.75
Sp.conductivity (2) µmho/cm	113.00	104.00	1.73	1.67	9.00	0.91	2.09	- 7.96
Tot.dissolved solids (1) mg/l (180°C)	338.00	470.67	32.02	6.80	7.18	0.72	1.67	39.25
Tot.dissolved solids (2) mg/l (180°C)	54.00	88.00		Single result				62.96
Tot.hardness (1) mg/l $CaCO_3$	136.00	145.00	13.23	9.13	1.18	0.12	0.27	- 6.62
Tot.hardness (2) mg/l $CaCO_3$	20.70	25.20		Single result				21.74
Ca (1) mg/l	40.60	41.10	0.56	1.35	1.56	0.16	0.36	1.23
Ca (2) mg/l	5.30	5.60		Single result				5.66
Mg (1) mg/l	8.40	10.30		Single result				22.62
Mg (2) mg/l	1.80	2.70		Single result				50.00
Na (1) mg/l	46.60	46.27	1.80	3.90	0.32	0.03	0.07	- 0.72
Na (2) mg/l	8.20	8.43	0.15	1.81	2.65	0.27	0.62	2.85
K (1) mg/l	9.80	9.27	0.32	3.47	2.87	0.29	0.67	- 5.44
K (2) mg/l	2.10	1.81	0.01	0.55	50.23	5.06	11.68	- 13.81
Tot.alkalinity (1) mg/l $CaCO_3$	74.70	74.40		Single result				- 0.40
Tot.alkalinity (2) mg/l $CaCO_3$	21.70	25.33	0.58	2.28	10.90	1.10	2.53	16.74
Cl (1) mg/l	87.90	97.20		Single result				10.58
Cl (2) mg/l	18.40	21.34	0.00	0.00	10.90	1.10	2.53	15.98
F (1) mg/l	1.30	1.17	0.04	3.57	5.55	0.56	1.29	- 10.26
F (2) mg/l	0.43	0.37	0.03	6.86	4.36	0.44	1.01	- 14.73
SO_4 (1) mg/l	93.60	95.00		Single result				1.50
SO_4 (2) mg/l	7.20	3.90	0.14	3.63	33.00	0.44	1.01	- 45.83
EPA 3 (1-2)								
F (1) mg/l	0.36	0.31	0.04	12.50	2.75	0.60	0.99	- 13.33
F (2) mg/l	2.30	2.18	0.04	2.05	6.00	1.30	2.16	- 5.22
NO_3 (1) mg/l N	0.22	0.39	0.19	47.99	2.02	0.44	0.73	76.36
NO_3 (2) mg/l N	10.10	9.83	0.32	3.24	1.22	0.44	0.73	- 2.73
EPA 4 (1-2)								
NH_4 (2) mg/l N	1.30	1.27	0.05	3.63	1.55	0.34	0.56	- 2.46
NH_4 (1) mg/l N	0.19	0.20	0.04	20.95	0.43	0.09	0.16	4.21
NO_3 (1) mg/l N	0.31	0.29	0.07	23.22	0.59	0.10	0.19	- 6.45
NO_3 (2) mg/l N	1.59	1.75	0.31	17.84	1.15	0.25	0.41	10.06
Ortho phosphate (1) mg/l P	0.03	0.03	0.00	15.97	1.00	0.22	0.36	- 6.67

Table 3 (continued)

Analyte	*True value*	*Mean value*	*Standard deviation*	*R.stand dev.*	t_c	*Confidence levels* % 99 *R*	% 95 *R*	*Percent error (%)*
Ortho phosphate (2) mg/l P	0.15	0.14	0.02	16.06	0.78	0.17	0.28	- 5.33
EPA 5 (1-2)								
Total P (1) mg/l P	0.14	0.15	0.01	6.90	1.00	0.17	0.31	3.57
Total P (2) mg/l P	0.93	0.87	0.19	21.65	0.64	0.11	0.20	- 6.45
EPA Heavy metals (1,2,3)								
As (1) µg/l	24.00	60.00	Single result					150.00
As (2) µg/l	182.00	400.00	Single result					119.78
As (3) µg/l	61.00	176.00	Single result					188.52
Cd (1) µg/l	6.50	8.17	1.76	21.50	1.64	0.17	0.38	25.64
Cd (2) µg/l	59.00	85.00	27.84	32.75	1.62	0.16	0.38	44.07
Cd (3) µg/l	27.00	29.33	2.31	7.87	1.75	0.18	0.41	8.64
Co (1) µg/l	30.00	28.67	5.51	19.21	0.42	0.04	0.10	- 4.44
Co (2) µg/l	348.00	340.00	17.32	5.09	0.80	0.08	0.19	- 2.30
Co (3) µg/l	96.00	89.00	12.17	13.67	1.00	0.10	0.23	- 7.29
Cu (1) µg/l	8.70	10.83	3.01	27.82	1.23	0.12	0.29	24.52
Cu (2) µg/l	374.00	397.00	5.20	1.31	7.67	0.77	1.78	6.15
Cu (3) µg/l	37.00	42.00	2.65	6.30	3.27	0.33	0.76	13.51
Fe (2) µg/l	796.00	813.33	23.09	2.84	1.30	0.13	0.30	2.18
Hg (1) µg/l	0.40	1.02	0.75	73.66	1.43	0.14	0.33	154.17
Hg (2) µg/l	7.60	7.03	0.52	7.40	1.89	0.19	0.44	- 7.46
Hg (3) µg/l	4.40	4.55	0.93	20.35	0.28	0.03	0.07	3.41
Mn (2) µg/l	478.00	443.33	37.86	8.54	1.59	0.16	0.37	- 7.25
Ni (1) µg/l	8.70	44.00	27.07	61.53	2.26	0.23	0.53	405.75
Ni (2) µg/l	165.00	176.67	32.15	18.20	0.63	0.06	0.15	7.07
Ni (3) µg/l	96.00	56.00	31.19	55.70	2.22	0.22	0.52	- 41.67
Pb (1) µg/l	30.00	31.17	2.75	8.84	0.73	0.07	0.17	3.89
Pb (2) µg/l	383.00	351.67	41.93	11.92	1.29	0.13	0.30	- 8.18
Pb (3) µg/l	113.00	111.00	13.53	12.19	0.26	0.03	0.06	- 1.77
V (1) µg/l	78.00	63.50	10.61	16.70	1.93	0.03	0.06	- 18.59
V (2) µg/l	848.00	670.00	42.43	6.33	5.93	0.03	0.06	- 20.99
V (3) µg/l	470.00	371.50	82.73	22.27	1.68	0.03	0.06	- 20.96
Zn (1) µg/l	6.10	29.50	2.18	7.39	18.60	1.87	4.32	383.61
Zn (2) µg/l	478.00	470.00	43.59	9.27	0.32	0.03	0.07	- 1.67
Zn (3) µg/l	26.00	40.67	14.01	34.46	1.81	0.18	0.42	56.41

Studend's t value : This value is calculated to compare the results of 3 or more determinations with true value.

$$t_c = \frac{|\mu - \bar{x}|\sqrt{n}}{s}$$

t_c = Student's t value, calculated from the equation above

m = True value

n = The number of replicate results

s = Standard deviation for n results

R value : Calculated from the following formula.

$$R = \frac{\text{Student's t, calculated}}{\text{Student's t, tabulated}} = \frac{t_c}{t_t}$$

Tabulated Student's t values are given in Table 4 (Laggley, 1971). It is evident from the equation given for t_c that when the mean is very close to the true value, t_c will turn out to be small. When t_c is smaller than t_t, R will be smaller than 1. As mean value has higher deviation from the true value, R will increase. When R is larger than one, systematic error is indicated at the confidence level selected as 95 % or 99 %.

% Error: Percent error for the mean with respect to the true value.

$$\% \text{ Error} = \frac{|(\bar{x} - \mu)|}{\mu} 100$$

Table 4 - Student's t, table values

Number of results, n	*Student's t value at indicated confidence level* 95 %	99 %
3	4.30	9.92
4	3.18	5.84
5	2.78	4.60
6	2.57	4.03

RESULTS

In the samples analyzed, Student's t test was applied to 54 results out of 65. Statistical evaluation could not be made for 11 results, as we had only a single result for the species involved. The 11 results were evaluated by indicating percent error only. R values have been used to investigate the presence of systematic errors at 95 % and 99 % confidence levels. As 99 % confidence levels evaluations give more optimistic results, 95 % confidence level, which in commonly used by analytical chemists, was employed as the basis of evaluation. At 95 % confidence level for 43 results out of 54, R values are less then 1; which correspond to 79.6 % of the total. Relative standard deviation for some of these values are fairly high. For example, the r.s.d. for Cd (1) is 21.5 % the R value is less than 1, and the result has passed the Studend's t test. These results show low precision but acceptable accuracy.

For 9 results, R value is higher than 1, but r.s.d. is less than 6 % .This group of results such as pH (1), specific conductivity, K (2), total alkalinity, Cl (2), F (1), SO_4 (2), Cu (2) show high precision but unaccaptable accuracy.

For 2 results, total dissolved solids (1), and Zn (1) the R value is higher than 1, and the r.s.d. is higher than 6 %. It is definite that, the methods involved for the results mentioned have errors higher than 10 %. However, for one of these determinations, namely Zn (1), the concentration level is very close to our detection limit, which was 5 ug/1.

As a result, no systemat ic error was observed for 43 results of the total of 54. For 9 results, failurein Student's t test is caused mainly by the relatively high precision obtained. In such occasions, increasingnumber of results, n, may lead to success in Student's t test, providing that x and s do show sufficient changes.

Regarding total dissolved solids (1), and Zn (1), the analytical methods employed require improvement.

In order to access the necessary dynamic character for any analysis laboratory, it is very important to run periodic trials by using methods similar to the ones presented in this study.

This should lead to some important decisions such as to improve or change the analytical methods employed.

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