A Comparative Study of Sample Preparation Methods for Stream Sediments Analyses Using ICP-AES

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Summary: Comparison between different digestion techniques is invariably subjective and designed to prove the superiority of one particular method over the other. Four sample preparation methods employing different digestion reagents were evaluated in term of digestion efficiency and accurate and precise analytical results in stream sediments of River Thames. The prepared solutions were subsequently analyzed for Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, MnO, and P_2O_5 using ICP-AES. The study showed that fusion with lithium metaborate ($LiBO_2$) was the best if SiO_2 is also required to determine. While HF-$HClO_4$ digestion method was equally good if SiO_2 is omitted. Digestion with HNO_3-$HClO_4$ or HCl-HNO_3 (aqua regia) was not found satisfactory for quantitative analysis and this method could only be applied for qualitative analysis of some elements. Three standard reference samples (KC10, KC12 and KC14) were introduced for accuracy and precision of analytical data.

Introduction

Analytical chemistry is the vital part of many disciplines of science, especially in research oriented activities all over the world. The application of digestion and analytical methods varies according to the nature of sample, instrument being used and the need of researchers [1, 2].

The continuous exploration for new mineral deposits is highly essential for the economic development of the country. Unfortunately, the progress of mineral exploration in Pakistan is quite slow. Geochemistry of stream sediment is a good method for prospecting ore deposits. The second author is an active member of a team who is engaged in such activities in the Balochistan area of Pakistan and published many articles [3, 4]. Present study is based on the analysis of 28 stream sediment samples of River Thames, England that have vast differences in element concentrations. The selection of digestion technique also depends upon the type of element present in the sediments [5]. This study will help to select suitable methods for digestion and analysis and the acquired knowledge may be utilized in Pakistan for better stream sediment survey.

The choice of digestion method and analytical instruments are mainly dependent upon solubility, detection limit, accuracy, precision, speed and cost of analysis [6, 7]. In present study ICP-AES method was adopted due to following reasons. It simultaneously measures major and trace elements with accuracy and has detection limit up to ng/l. It does not require further dilution so that this method is free from dilution error [8]. It has a wide range of applications in geological samples at rapid speed and cost effective manner [9, 10].

Results and Discussion

Results of 14 samples (depth and surface) by using four different digestion methods are given in tables-3 to 6. The data of three standard reference samples (KC10, KC12 and KC14) is also given in Table-2. The results of analytical data of different digestion methods is discussed below with reference to nature of element, its abundance in stream sediments and oxidizing power of different acids.

Table 1: Working conditions of ICP-AES (Perkin-Elmer), model 3300RL

Parameters	Conditions
Gas flow Plasma	15 l/min
Auxiliary gas flow (ar)	0.5 l/min
Neubulizer flow	0.8 l/min
Power	1.3 kW
Flow rate of solution	1.5 ml/min

Table 2: Standard Rock Data (%). (provided by the Department of Geology, Royal Holloway University, London, UK).

Oxide	KC 10	KC 12	KC 14
Al_2O_3	17.40	15.20	11.60
Fe_2O_3	9.90	2.80	1.68
MgO	7.70	1.20	0.01
CaO	11.90	1.80	0.21
Na_2O	2.40	4.20	3.78
K_2O	0.20	4.30	4.78
TiO_2	0.84	0.35	0.13
P_2O_5	0.09	0.12	0.00
MnO	0.13	0.05	0.02

Table 3: Concentrations of elements in the stream sediments of River Thames and standards using HF-$HClO_4$ digestion method (%).

Sample #	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
KC10	18.08	10.11	7.86	11.37	2.55	0.24	0.96	0.04	0.14
KC12	15.32	3.19	1.25	1.82	4.15	4.10	0.35	0.10	0.04
KC14	11.75	2.22	0.02	0.17	3.85	4.86	0.14	0.00	0.03
1D	13.05	6.16	2.53	2.30	1.25	2.81	0.73	0.15	0.03
1S	5.75	2.99	0.99	4.93	1.35	1.51	0.42	0.14	0.03
2D	5.23	2.60	0.85	4.91	1.04	1.51	0.35	0.10	0.03
2S	5.57	2.87	0.95	4.85	1.27	1.53	0.45	0.14	0.03
3D	12.32	5.78	2.05	6.63	1.79	2.45	0.64	0.13	0.06
3S	4.72	2.50	0.76	5.15	0.94	1.40	0.31	0.11	0.03
4D	7.62	4.13	1.19	4.37	1.16	1.81	0.46	0.11	0.03
4S	5.79	2.99	0.96	5.94	1.24	1.59	0.32	0.16	0.03
5D	13.71	6.30	1.95	1.04	1.67	2.77	0.70	0.12	0.02
5S	11.99	6.05	1.81	2.79	1.52	2.38	0.62	0.23	0.04
6D	6.53	4.66	1.18	5.46	1.17	1.55	0.35	0.35	0.05
6S	6.41	4.33	1.07	4.74	0.98	1.55	0.35	0.22	0.06
7D	9.33	5.15	1.59	7.40	1.18	1.80	0.56	0.41	0.06
7S	8.81	5.13	1.48	7.21	1.11	1.72	0.58	0.55	0.06
8D	11.38	7.26	1.83	4.84	1.31	2.07	0.56	0.53	0.09
8S	10.29	5.91	1.72	4.86	1.29	1.90	0.52	0.45	0.05
9D	7.91	3.92	1.35	5.97	1.57	1.81	0.44	0.21	0.05
9S	6.18	3.35	1.04	5.67	1.18	1.59	0.38	0.26	0.04
10D	7.09	3.93	1.12	5.10	1.26	1.64	0.42	0.32	0.04
10S	4.74	2.72	0.66	4.21	0.94	1.39	0.36	0.23	0.04
11D	4.31	2.25	0.75	4.43	0.96	1.05	0.31	0.13	0.02
11S	4.45	2.47	0.78	8.28	1.07	1.32	0.38	0.19	0.04
12D	5.22	2.71	0.83	6.07	1.02	1.47	0.36	0.13	0.03
12S	5.62	2.98	0.96	6.42	1.23	1.54	0.48	0.18	0.04
13D	1.40	1.66	0.13	18.00	0.12	0.53	0.09	0.31	0.04
13S	2.49	2.38	0.23	19.98	0.17	0.81	0.17	0.30	0.04
14D	1.60	1.55	0.14	17.69	0.14	0.56	0.10	0.27	0.03
14S	1.21	1.32	0.10	12.97	0.12	0.51	0.08	0.22	0.02

Al_2O_3

Aluminum is the second most abundant oxide (Al_2O_3) in the earth crust [11] and it has similar position in the stream sediments and soils [12]. In the fine fraction of stream sediments Al occurs as clay minerals, however in the coarse portion feldspars and feldspathoids along with garnet, kyanite etc are common.

The results of digestion by HNO_3-$HClO_4$ are very high in contrast to other methods. The error in sample 7S and 11D is more than 3 times, however majority of analysis shows double concentration (Table-5). It is not simple to argue for the high concentration of Al. Possibly both these acids have very strong oxidizing power which cause interference of other elements that have variable valences. The data obtained by aqua regia show slightly lower values, probably because nitrosyl chloride (NOCl) has poor power to ionize Al [13]. Lithium meta borate and HF-$HClO_4$ methods are quite satisfactorily and are close in values (Fig. 1A). It has advantage to break the matrix of the sample [13].

Fe_2O_3

The concentration of total iron (Fe_2O_3) is about 6.64 % in the crustal rocks while it is about 3.00 % in the soil [12]. In the stream sediments Fe occurs as hematite, limonite, magnetite and siderite, however presence of iron bearing igneous and metamorphic minerals is also possible. In contrast to Al, aqua regia method of digestion gives high results of same stream sediments (Fig. 1A). Leaching with aqua regia may cause inconsistence results [1]. Nitric-perchloric acids also show high results of Al_2O_3, Fe_2O_3 and K_2O. The high value is probably due to interference of other elements. The data obtained by $LiBO_2$ fusion method is close to standard sample (KC10, KC12 and KC14) therefore this method represents true picture of element distribution in the stream sediments.

CaO and MgO

Both Ca and Mg belong to alkaline earth metal group and their abundance in the crustal rocks is 4.61 and 2.72 % respectively. Limestone, dolomite,

Table 4: Concentrations of elements in the stream sediments of River Thames and standards using aqua regia digestion method (%).

Sample #	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
KC10	27.18	26.48	17.94	12.92	2.42	0.35	0.31	0.18	0.20
KC12	9.53	12.2	5.75	1.64	0.38	3.91	0.44	0.47	0.13
KC14	2.06	7.41	0.01	0.70	0.62	1.00	0.16	0.01	0.05
1D	11.06	18.62	8.23	10.05	3.87	2.30	0.13	0.60	0.11
1S	5.82	10.57	3.78	22.32	4.94	1.50	0.09	0.62	0.11
2D	4.97	9.28	3.23	22.09	3.03	1.28	0.09	0.41	0.09
2S	5.24	9.88	3.71	22.63	4.23	1.37	0.09	0.64	0.11
3D	11.57	18.74	6.88	28.94	6.63	2.75	0.11	0.51	0.23
3S	4.88	9.43	3.08	24.17	2.86	1.26	0.09	0.51	0.10
4D	7.26	14.53	4.42	22.18	3.98	2.02	0.08	0.51	0.12
4S	6.00	10.62	3.60	26.62	3.68	1.49	0.09	0.66	0.12
5D	13.03	20.62	6.32	4.49	5.79	3.21	0.09	0.47	0.09
5S	11.64	20.94	6.16	12.65	5.68	2.65	0.08	0.89	0.16
6D	6.12	16.77	4.25	24.66	4.17	1.52	0.08	1.50	0.23
6S	6.55	15.75	3.81	21.83	2.88	1.57	0.07	0.96	0.21
7D	7.88	16.46	5.16	33.05	4.26	1.65	0.06	1.47	0.21
7S	8.05	16.03	4.75	32.65	3.67	1.67	0.06	2.44	0.20
8D	9.05	24.58	5.81	22.51	5.13	1.96	0.05	2.36	0.40
8S	9.06	19.57	5.55	22.64	4.92	1.92	0.05	1.98	0.21
9D	5.67	12.15	4.60	27.04	5.38	1.33	0.06	0.92	0.18
9S	4.67	11.02	3.66	25.18	3.32	1.05	0.06	1.13	0.16
10D	4.74	12.89	3.99	23.38	3.79	1.10	0.07	1.41	0.18
10S	2.67	8.25	2.47	19.00	1.74	0.68	0.05	0.89	0.13
11D	5.72	11.43	4.27	32.24	5.81	1.40	0.07	0.86	0.14
11S	3.30	7.83	2.95	36.09	3.25	0.86	0.06	0.81	0.12
12D	4.37	9.17	3.12	27.49	3.14	1.05	0.07	0.59	0.11
12S	4.48	9.45	3.58	30.05	3.82	1.08	0.07	0.78	0.13
13D	1.73	6.53	0.55	78.57	0.12	0.31	0.03	1.37	0.14
13S	2.94	8.90	0.89	87.68	0.16	0.52	0.03	1.24	0.16
14D	1.63	5.94	0.55	79.21	0.15	0.25	0.02	1.18	0.15
14S	1.27	5.32	0.45	58.12	0.11	0.26	0.02	0.84	0.10

magnesite and gypsum are the main contributors of Ca and Mg in the sediments and are easily digested in acids or aqua regia. Calcium or magnesium bearing igneous and metamorphic rocks require either fusion or HF-$HClO_4$ digestion for their decomposition. Stream sediments with high amount of Ca will cause some low results while treating with HF-$HClO_4$ [10]. Stream sediments data of present study also reflects low CaO values for HF-$HClO_4$ treated samples in comparison to $LiBO_2$ fusion method (Table 6). Result of aqua regia and HNO_3-$HClO_4$ are very poor and high respectively (Fig. 1A & Table 4). It is important to note that sample numbers 13 and 14 (S&D) show extraordinary amounts of CaO in the stream sediments (50-87 %), such high values are not possible in any geomaterials even in pure lime.

Digestion with aqua regia and HNO_3-$HClO_4$ are also not recommended for MgO in the stream sediments because both show very high result. The results obtained from $LiBO_2$ and HF-$HClO_4$ is quite satisfactory. The extent of error is quite low as compared to CaO, because MgO do not form complex (CaF_2) with F like Ca [14].

Na_2O and K_2O

Sodium and potassium are important constituents of feldspars, mica and clay minerals. Lithium meta borate ($LiBO_2$) and HF-$HClO_4$ methods are equally good, additionally $HClO_4$ does not has depressant effect upon emission spectrophotometry of the alkalis [13]. Estimation of Na_2O by aqua regia gives maximum readings (Table 5), while high value of K_2O was observed by HNO_3-$HClO_4$ method. The result of K_2O by HF-$HClO_4$ for standard sample (KC12) was quite low (Fig. 1B & Table 3).

TiO_2

The result of TiO_2, fused with $LiBO_2$, was in agreement with the certified values of standards KC10 (Fig. 1B). Extraction with aqua regia gives very low result ((0.02-0.08 %). The low values of Ti, probably is due to its strong refractory nature and it do not digest by aqua regia [13]. The rest two methods (HF-$HClO_4$ and HNO_3-$HClO_4$) are average, except the former will interfere if fluoride ions are not properly removed during digestion [13].

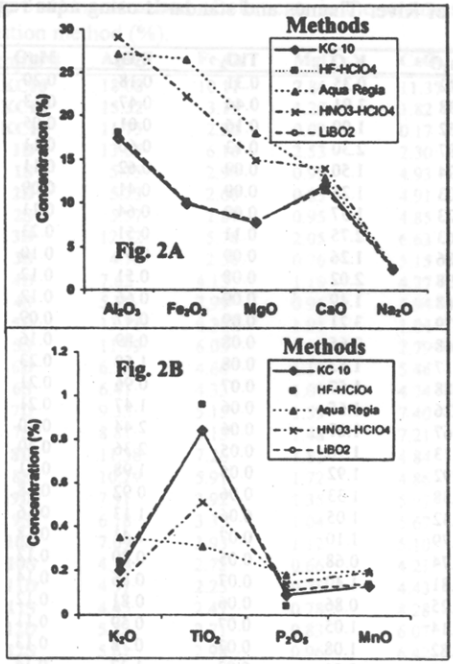

Fig. 1: Comparison of results of four different methods against standard KC 10.

P_2O_5 and MnO

Geochemically phosphorus and manganese are classified as minor elements. The average crustal abundance is 0.2 and 0.13 % respectively. Their distribution in the stream sediments varies between 100 and 5000 ppm with respect to exposed rocks in the area [15]. Their availability in the stream sediments also depends upon the pH and Eh of the deriving water. The average of 28 samples from our study area have 0.25% (Table-3 and 6), which show no anomaly in the area. The result obtained from aqua regia digestion is once again high in contrast to other methods (Fig. 1B & Table-4).

Values of MnO of different stream sediments is quite consistent i.e. 0.03 %. High values are recorded both for standards and samples, treated with aqua regia.

Experimental

Sample Sites

The study area lies east of London (Fig. 2A) along River Thames, its tributaries and Medway area (Fig. 2B). River Thames flows towards east and



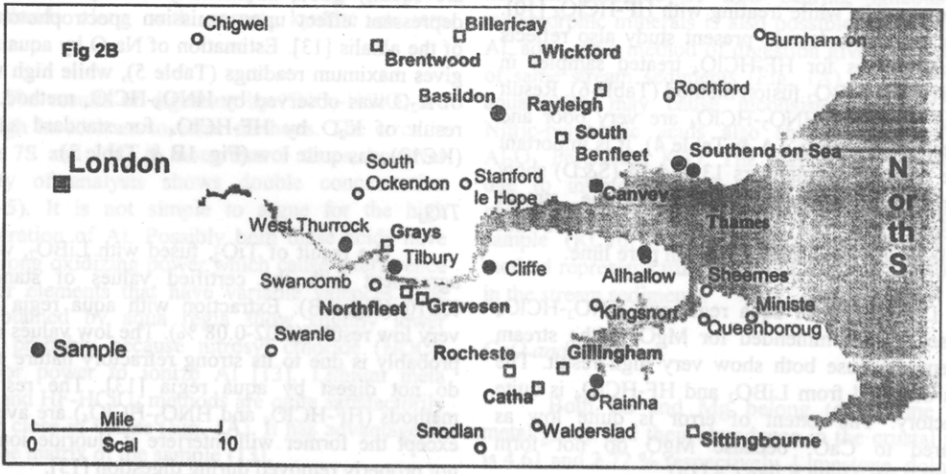

Fig. 2: Map of the United Kingdom showing study area (2A). Map of eastern London showing sample sites (2B).

Table 5: Concentrations of elements in the stream sediments of River Thames and standards using HNO_3 $HClO_4$ digestion method (%).

Sample #	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
KC10	29.05	22.11	14.82	13.90	2.52	0.14	0.51	0.14	0.19
KC12	8.73	9.86	4.46	2.07	0.34	3.11	0.49	0.35	0.11
KC14	1.46	4.62	0.00	1.70	0.63	0.88	0.08	0.01	0.03
1D	23.87	17.84	7.72	8.08	2.92	4.07	0.33	0.45	0.10
1S	10.70	9.94	3.52	18.10	4.09	1.97	0.20	0.51	0.09
2D	5.49	6.93	2.43	15.62	1.97	1.17	0.07	0.31	0.07
2S	10.98	9.33	3.49	18.19	3.46	2.05	0.29	0.52	0.10
3D	26.72	17.64	6.58	22.63	5.21	4.93	0.40	0.41	0.19
3S	8.07	8.08	2.66	18.30	2.16	1.54	0.18	0.38	0.08
4D	18.21	14.49	4.61	18.92	3.40	3.38	0.34	0.44	0.12
4S	9.48	8.82	3.01	19.95	2.73	1.78	0.18	0.50	0.09
5D	30.19	21.17	6.79	3.94	5.10	4.67	0.32	0.42	0.09
5S	33.77	20.87	6.60	10.43	4.73	5.41	0.58	0.76	0.15
6D	15.28	15.81	4.20	20.50	3.38	2.61	0.29	1.23	0.20
6S	16.33	14.72	3.91	18.32	2.51	2.76	0.33	0.79	0.19
7D	26.22	15.75	5.89	27.81	3.76	4.32	0.46	1.25	0.14
7S	26.50	17.50	5.39	28.04	3.31	4.12	0.66	1.99	0.19
8D	34.04	24.81	6.54	18.03	4.20	3.97	0.52	1.89	0.33
8S	28.26	19.30	5.94	17.93	3.96	4.28	0.49	1.53	0.18
9D	22.19	13.58	5.00	22.69	4.57	3.63	0.64	0.77	0.16
9S	14.46	11.43	3.81	21.26	2.87	2.36	0.42	0.96	0.14
10D	16.32	13.15	4.01	18.90	3.04	2.65	0.50	1.13	0.16
10S	6.81	8.72	2.53	16.64	1.65	1.26	0.21	0.81	0.12
11D	14.46	11.38	4.16	26.09	4.56	2.46	0.32	0.72	0.13
11S	8.79	8.39	3.04	31.95	2.94	1.59	0.27	0.70	0.12
12D	10.93	8.81	3.03	22.95	2.63	1.88	0.35	0.49	0.10
12S	13.01	9.69	3.53	25.05	3.18	2.19	0.55	0.66	0.12
13D	0.60	1.67	0.12	18.04	0.03	0.11	0.01	0.33	0.03
13S	5.61	8.36	0.95	77.83	0.14	0.85	0.13	1.08	0.14
14D	3.31	5.60	0.61	66.26	0.11	0.49	0.08	1.04	0.13
14S	1.96	4.90	0.47	50.53	0.09	0.37	0.05	0.80	0.09

finally falls into North Sea. Seven areas were selected for present study. Southend (samples 1 & 2), Allhallows (samples 3 & 4), Cliffe (samples 5 & 6), Rainham (samples 7 & 8), Tilbury (samples 9 & 10), Canvey Island (samples 11 & 12), and near Grays (samples 13 & 14). From each location, surface samples (numbers with S) as well as up to 20 cm deep samples (numbers with D) were taken. The sample sites were selected on the basis of nature and type of bedrock, soil and drainage system of the area.

Sample Preparation

The samples were dried at 105°C, pulverized in a grinding mill and sieved through 200-mesh screen. The minus 200 mesh fraction was selected for chemical analysis. Following four digestion methods were adopted for sample preparation.

i) HF-$HClO_4$: Samples were digested using a mixture of HF-$HClO_4$ in 1:2, in the Teflon crucibles. Keep the mixture on hot plate at 195°C till dryness. Acidify it with few drops of HNO_3. Prepared 1 % solution using distilled water.

ii) HCl-HNO_3 (Aqua regia): Samples were digested in aqua regia. Kept it on hot plate at 80°C for 20 minutes. Later, cooled, filter and prepare solution of 1 %.

iii) HNO_3-$HClO_4$: Samples were treated with concentrated perchloric and nitric acids, with a ratio of 7:3. After heating to dryness the residue was leached with 6M nitric acid and prepared 1 % solution [16].

vi) $LiBO_2$: Samples were fused in Pd/Au alloy crucibles using lithium meta borate as flux in 1:3 ratio. Treat the fused mixture in 250 ml teflon beaker with 30 % HNO_3. Finally, prepare the solution as usual.

ICP-AES Analysis

The solutions were analyzed for Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O5 and MnO using ICP-AES (Perkin-Elmer), model 3300RL, at the Department of Geology, Holloway University of London, England. The instrumental was set

Table 6: Concentrations of elements in the stream sediments of River Thames and standards using $LiBO_2$ digestion method (%).

Sample #	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
KC10	17.66	10.05	7.78	11.38	2.47	0.22	0.83	0.11	0.14
KC12	15.43	3.21	1.26	1.82	4.26	2.28	0.37	0.14	0.04
KC14	12.41	2.20	0.01	0.16	3.74	4.77	0.12	0.03	0.03
1D	12.77	5.68	2.49	2.27	1.36	2.74	0.81	0.16	0.03
1S	5.88	2.87	1.04	4.98	1.32	1.46	0.56	0.15	0.03
2D	5.32	2.33	0.87	4.96	1.04	1.44	0.52	0.10	0.03
2S	5.81	2.84	1.02	5.02	1.31	1.52	0.63	0.15	0.03
3D	6.49	4.19	1.19	5.51	1.16	1.51	0.43	0.34	0.05
3S	6.68	4.39	1.13	5.20	0.93	1.47	0.45	0.22	0.05
4D	7.97	4.01	1.31	5.00	1.20	1.81	0.62	0.14	0.03
4S	5.80	2.74	0.98	5.99	1.16	1.49	0.41	0.16	0.03
5D	13.74	6.16	1.99	1.05	1.65	2.76	0.84	0.15	0.02
5S	12.01	5.64	1.85	2.83	1.54	2.37	0.75	0.23	0.04
6D	6.44	4.20	1.19	5.43	1.11	1.45	0.43	0.33	0.05
6S	6.42	4.36	1.09	4.92	0.94	1.52	0.47	0.22	0.54
7D	9.35	5.12	1.63	7.52	1.18	1.80	0.68	0.41	0.05
7S	8.62	4.78	1.50	7.43	1.05	1.67	0.69	0.53	0.05
8D	11.80	7.25	1.91	5.03	1.36	2.18	0.67	0.57	0.09
8S	10.26	5.59	1.73	5.07	1.28	1.88	0.62	0.46	0.05
9D	7.80	3.81	1.37	6.09	1.51	1.74	0.58	0.23	0.04
9S	6.16	3.28	1.06	5.77	1.17	1.54	0.55	0.28	0.04
10D	7.27	3.70	1.17	5.25	1.27	1.65	0.55	0.34	0.04
10S	4.61	2.61	0.68	4.28	0.87	1.32	0.48	0.21	0.03
11D	6,79	3.39	1.20	7.14	1.50	1.64	0.64	0.22	0.04
11S	4.60	2.35	0.83	8.29	1.09	1.32	0.58	0.20	0.03
12D	5.22	2.50	0.85	6.16	0.96	1.39	0.49	0.15	0.03
12S	5.74	2.96	1.04	6.76	1.15	1.47	0.69	0.20	0.04
13D	1.31	1.52	0.15	17.40	0.03	0.45	0.09	0.27	0.03
13S	2.58	2.50	0.26	20.28	0.10	0.80	0.23	0.30	0.04
14D	1.54	1.54	0.17	17.48	0.05	0.50	0.13	0.28	0.03
14S	1.35	1.57	0.14	13.13	0.04	0.54	0.18	0.23	0.03

according to the manufacture's instructions while working conditions were set as given in table-1. The analytical results were monitored by using three different standard reference samples (Table-2).

Conclusions

The results obtained by four different digestion methods have provided valuable information for choosing precise and accurate method for the analysis of stream sediments in varying geological conditions. The paper also concludes the effectiveness of different analytical techniques being applied in the field of exploration geochemistry. Present study also furnishes the information regarding abundance, mineralogy, solubility and mobility of different elements in relation to assorted digestion techniques.

The comparative study for the digestion of stream sediments and soils shows that fusion with $LiBO_2$ gives best results (Fig. 1). This method has an opportunity to estimate SiO_2 in addition. Digestion with HF-$HClO_4$ is equally good with little variations and cannot be applied if SiO_2 is required to measure. The rest two methods (HNO_3-$HClO_4$ and aqua regia) are not satisfactory. The standards and sediment samples, treated with aqua regia shows very high amount of Fe_2O_3, MgO, CaO, Na_2O, TiO_2, MnO, and P_2O5. Sample digested with HNO_3-$HClO_4$ also gives high results of Al_2O_3, K_2O and Fe_2O_3.

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