DETERMINATION OF TRACE METALS IN MAHAWEEL RIVER SEDIMENTS BY ACID EXTRACTION

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Abstract

In this study, a boiling mixture of acids (20% HCl + 80% HNO_3) was used to extract trace metals from sediments for Mahaweel River (branch of Euphrates). The elements of interest included Na, Mg, Ca, Cr, Cu, Pb, Hg and Ni, all of which can be determined by electro thermal atomic absorption spectrometry (ETAAS). High recoveries percentage 96, 97, 99, 99, 97.5 and 95 for Na, Mg, Ca, Cr, Cu, and Pb, respectively. The relative standard deviation of the method is less than 3%. Calibration graphs for Pb, Ni and Cr were found to be linear between 100-250, 80-180, 180-250 ng/mL, respectively However, when the acid extraction method was applied to some selected sediments, the resulting trace metal concentrations, although reproducible. Apparently SRM-1645 provided too favorable an assessment of the true accuracy of the method with ordinary sediments.

Keywords: electro thermal atomic absorption spectrometry, Acid extraction, Sediments.

Introduction

Trace metal determination in sediments commonly involve some type acid extraction followed by flame photometer(1, 2) and atomic absorption analysis(3, 4). Such methods are reasonably rapid and inexpensive, and many workers have demonstrated that they provide precision and reproducibility satisfactory for environmental monitoring purpose(5-7). In this study, several approaches have been used to evaluate completeness precision, and accuracy of an acid extraction, electro thermal atomic absorption spectroscopy (ETAAS) method and the method has been tested with Mahaweel River sediments standard recently issued by the United State National Bureau of Standards (NBS-SRM-1645)(8,9), and it has also been tested by comparison with a totally independent method involving fusion of the sample in lithium metaborate and subsequent determination by emission spectroscopy(10).

Experimental

1-Reagent:

The concentrated acids are hydrochloric acid (HCl; F.W. 36.45; density. 1.184; 37% HCl; ≈ 12M), nitric acid (HNO_3: F.W.63.01, density.1.41, 65% HNO_3) and sulfuric acid (H_2SO_4 F.W. 98.07, density, 1.83, 94% H_2SO_4). The salts are copper (II) sulfate, anhydrous ($CuSO_4$; F.W. 159.60), magnesium chloride, anhydrous ($MgCl_2$; F.W. 95.22), calcium chloride, anhydrous ($CaCl_2$; F.W. 110.99), sodium chloride (NaCl: F.W. 58.45) potassium dichromate ($K_2Cr_2O_7$: F.W.294.19), lithium metaborate ($LiBO_2$ F. W. 49.75), lead chloride ($PbCl_2$: F.W. 278.10), mercury chloride ($HgCl_2$: F. W.271.52) and lithium nitrate ($LiNO_3$: F. W. 68.94)]. All chemicals and solvents were an analytical reagents grade obtained from BDH, Fluka and Aldrich companies. The deionized distilled water was used for all standard solutions were prepared using deionized distilled water in a manner similar to that Dean or Rains(10). All samples had been collected by using a Ponar grab sampler. The randomly selected samples were extracted and analyzed in duplicate.

2- Apparatus:

Electro thermal atomic absorption spectroscopy with several instruments Shimadzu 12001 and instrumentation laboratories 512 using for analysis of the sample extracts. All Pyrex glassware and polyethylene bottles washed in 14 M sulfuric acid. The primary wavelength for Ca, Mg, and Na was used to obtain better precision, but a secondary wavelength for Ni was used to obtain better precision. Chromium analysis was done by using a lean flame to remove interferences.

3- Procedure:

The sediments sample for Mahaweel River were dried in oven between 80-120 °C for two days and then ground in a mullet corundum ($3Al_2O_32SiO_2$) mortar. Approximately 10-50 g was weighed to the nearest 0.001g on a mettler balance and placed in a 500 mL boiling flask. A 20 mL of concentraed HCl and 80 mL concentrated nitric acid placed in the flask, reflux condenser (25-35 cm) was placed on the flask. The contents were refluxed on a hot plate for two hours, with vigorous boiling for remote mixing. After cooling the contents of the flask were transferred to a centrifuge and centrifuged for 15 min. Then filtered through whatman No-1 filter paper. The remaining sediments were washed two times with 20 mL of water. The filtrate and washing solutions were collected in a 500 mL beaker. The resulting solution was reduced to approximately 25 mL by heating on a hot plate. Then, transferred to 50 mL volumetric flask, and completed to volume with 5% nitric acid Fig.(1). The extracts were stored in a polyethylene bottles.

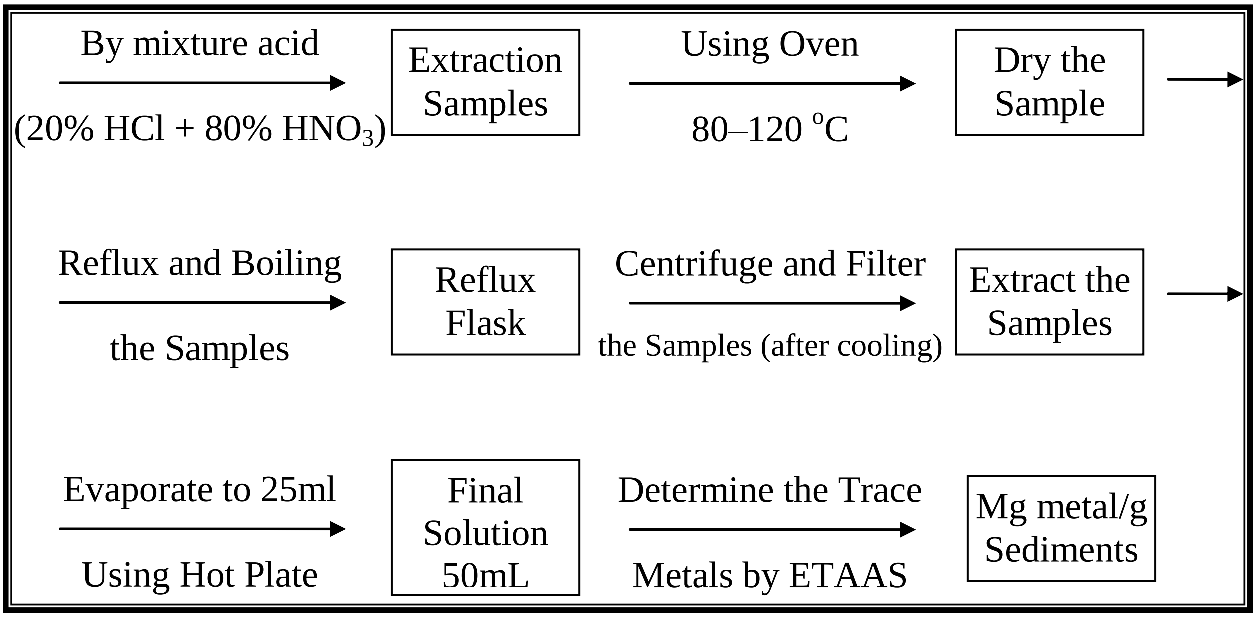

Fig.(1) : Procedure for Trace Metals Extraction.

Trace metals in various sediments samples were also determined by fusin the samples with lithium metaborate(11), dissolving the resulting glass bead in 5% nitric acid and using direct current argon plasma emission spectrometry (ICP) was used to determine the trace metal of the solutions. The dried sediments were fused with 0.5 g of lithium metaborate in a graphite crucible between 800-1000 ºC for approximately 15-20 min.

The molten lithium metaborate glass bead was poured into 200 mL beaker contain 100 mL of 5% HNO_3. The beaker content were stirred between 10-15 min. Then the solution was transferred to a polyethylene bottle. Each sediment sample was fused in triplicate. Working standards were prepared by dilution of the previously described stock solutions using lithium nitrate solution in 5% HNO_3 so that, the concentration of lithium salt in the samples matched in standard.

4- Procedure for calibration curves:

Calibration graph for Pb, Ni, and Cr were found to be linear between 100-250, 80-180, 180-250 ng/mL respectively. Table (1) shows the absorbance versus the concentration of Pb, Ni and Cr.

Table (1)
The absorbance of Pb, Ni and Cr versus the concentration.

ng/mL Pb	Absorbance	ng/mL Ni	Absorbance	ng/mL Cr	Absorbance
75	0.31	50	0.331	140	0.083
100	0.295	80	0.320	160	0.512
125	0.380	100	0.418	180	0.525
150	0.420	125	0.520	200	0.709
200	0.591	150	0.625	220	0.855
250	0.712	180	0.771	240	1.071
300	0.625	200	0.725	250	1.125
350	0.699	250	0.798	270	1.035

Results and Discussion

Boiling of solutions increase the metal recovery between 8-12% when compared to shaking on a mechanical shaker at 80ºC using nitric acid alone which was not adequate to obtain proper result therefore addition of 20% HCl increases the efficiency of extraction. Table (1) shows the conditions of (ETAAS) method. Thus, refluxing with mixture of acids (20% HCl + 80% HNO_3) increased recovery by approximately 6-8% over nitric acid alone

Trefry et al.(12) showed an increase in extraction of up to 15% by adding 6 N HCl to 16 N HNO_3, but in this work, (20% HCl + 80% HNO_3) of acids mixture comparable to aqua regia in the completeness of extraction, but it has the advantage of lower blanks than aqua regia. The effect of the sediment to acid ratio (20% HCl + 80% HNO_3) was tested for extraction by using of the Mahaweel River sediment for three hours would probably have been sufficient, but a time of four hours was chosen to guaranty the result.

Table (2)
The Wavelength of Metals Absorbance by ETAAS.

No.	Metals ions	Elements name	Solution analyzed	Wave length (nm)	Comments
1	Na^+	Sodium	Diluted	589.00	Diluted to 100 mL
2	Mg^{++}	Magnesium	Diluted	285.20	Diluted to 50 mL
3	Ca^{++}	Calcium	Diluted	422.70	Diluted to 100 mL
4	Cu^{++}	Copper	Extracted	324.00	Background correction used
5	Pb^{+2}	Lead	Extracted	217.00	Background correction used
6	Hg^{+2}	Mercury	Nil	253.65	------------
7	Cr^{+3}	Chromium	Extracted	358.00	------------
8	Ni^{+2}	Nickel	Nil	341.00	------------
9	Cd^{+2}	Cadmium	Extracted	228.00	Background correction used

In Table (3), shows the National Bureau of Standards (NBS) certified values with 95% confidence limits have been shown. Our procedure showed results, in most cases, are within the confidence limits given by the NBS, except in the case of mercury and nickel which are (nil).

Table (3)
Extraction Result for the National Bureau of Standard Sediment Standard (NBS-SRM-1645) and for the Samples.

Metals	**NBS-SRM-1645**					**Samples**			
	Acid Mixture, %	**Recovery, %**	**Er, %**	**RSD, %**	**NBS. Values**	**Acid Mixture, %**	**RSD, %**	**Recovery, %**	**Er, %**
Na	4.6	96	3.9	2.3	4.71	4.8	2.2	97	3.1
Mg	5.2	97	2.8	2.4	5.29	5.6	2.6	97	2.9
Ca	5.2	99	0.9	1.1	5.30	5.6	0.9	99	0.9
Cr	3.1	99	0.9	1.1	3.08	4.1	0.9	99	0.9
Cu	2.9	97.5	2.5	2.1	2.86	3.2	2.9	98	1.2
Pb	3.6	95	4.8	3.1	3.72	5.2	1.8	98	1.2

***Note*:**
These results at 95% confidence limits and the number of samples used is seven.

The acid extracts of NBS sediment were also analyzed for sodium, magnesium, calcium, copper, chromium, and lead. Table (3) shows RSD % for metals. The results are excellent and agreement with the values determined by ETAAS method. But ETAAS cannot record the concentration of Ni and Hg because they are nil or very low. NBS-SRM-1645 could not be reliably analyzed by the fusion-ICP method because an insoluble magnetic phase believed to be chrome magnetite formed during fusion in lithium metaborate to eliminate the possibility that falsely high values for Ni and Hg by fusion–ICP, rather than falsely low values (or nil) by extraction ETAAS method, were responsible for the apparent poor recoveries from the sample. We followed the U.S. Geological Survey's marine mud standard (MAG-1).

The result for the fusion-ICP method are shown in Table (4) and matched the values reported by Flanagan (Flanagan's values are averages obtained from round-robin analysis rather than certified values based on concordant analysis from two or more independent methods as in the case of NBS-SRM-1645).

Further, evaluation of recovery and reproducibility was made by analyzing six randomly selected samples twice by the acid extraction method and once by the fusion method. Table (4) shows the results from randomly selected sample with ppm concentration of dry sediment.

Table (4)
Results from Randomly Selected Samples of Dry Sediments.

No.	Metals	Mud Extraction ppm	Sand Extraction ppm	Number of Samples test	Total Number of Samples
1	Na	36 36 34	33 34 31	3	6
	Average	35.3	32.67		
2	Mg	26 26 25	25 20 23	3	6
	Average	25.67	22.67		
3	Ca	42 43 41	42 44 46	3	6
	Average	42	44		
4	Cr	0.1 0.1	0.09 0.08	2	4
	Average	0.1	0.085		
5	Cu	1.3 1.1	1.1 1.0	2	4
	Average	1.2	1.05		
6	Pb	1.1 1.2	0.9 1.4	2	4
	Average	1.15	1.15		
7	Hg	Nil	Nil	3	6
8	Ni	Nil	Nil	3	6

An overall comparison for six elements is Table (5). The percent recoveries were calculated for the acid extraction-ETAAS method results by assuming that the fusion-ICP method yielded true total metal concentration. Sodium, magnesium, calcium, copper, chromium, and lead have been rejected in Table (5) because the fusion-ICP method was insufficiently sensitive to determine these elements.

As can be seen, the recoveries vary considerably for each metal. If the samples were separated according to grain size into mud and sands, the recoveries are high (~> 50%) for mud but low for sands.

Table (5)
Comparison of Recovery for Acid Extraction and Fusion Methods.

Samples Types	Recovery %											
	Na		Mg		Ca		Cu		Cr		Pb	
	Acid extraction	Fusion	Acid extraction	Fusion	Acid extraction	Fusion	Acid extraction	Fusion	Acid extraction	Fusion	Acid extraction	Fusion
Muds	85	84.6	80.6	83.7	97	98.1	95.4	97.6	93.7	99.2	96.4	96.6
Sands	85.3	84.9	80.4	84.3	97.5	98.6	96.3	99.2	94.9	99.4	96.3	96.5
Mixtures	84.2	83.8	89.3	83.1	96.4	97.5	96.4	99.4	93.8	98.3	95.2	95.4

The first truly calibrated material of this type available for sediments is the recently issued SRM-1645. When this reference material was used to test the accuracy of the acid extraction-ETAAS method of sediments, very encouraging results were obtained.

The low recoveries reported in some cases by the acid extraction-ETAAS method. Table (5) because the ionized for some Na and Mg atoms in the atomization process. The excellent recovery takes place of Ca, Na, and Pb in the sand samples and all samples in the acid extraction.

Table (6)
Comparison of Acid Extraction and Borated Fusion Results for Calibration Curves from Magnesium and Calicum.

ppm Concentration	Magnesium Extraction %		Calcium Extraction %	
	Acid Extraction %	Borate Fusion %	Acid Extraction %	Borate Fusion %
100	6	13.5	3	14
200	15	26	14	31
300	24	35	25	46
400	34	51	36	63
500	50	65	53	77.5
600	53.5	71	57	85

The latter data in Table (6) have been plotted in Fig.(2) and Fig. (3) to show that the size of the magnesium and calcium deficits in the acid extraction data increases as the amount of magnesium and calcium present in the samples respectively.

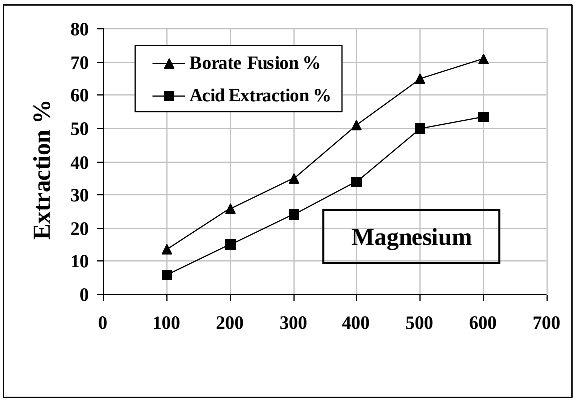

Fig.(2): Acid Extraction Results and. Borate Fusion Results for Six Randomly Selected Samples for Magnesium concentration versus recovery%.

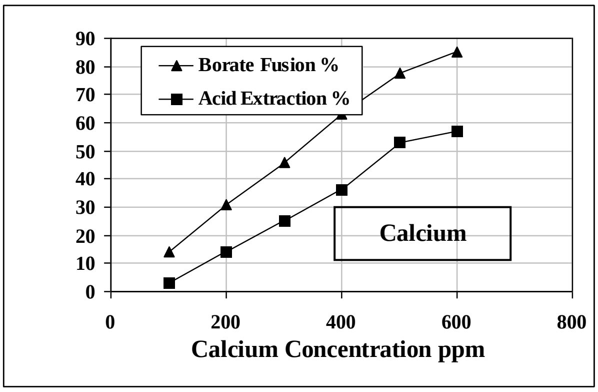

Fig.(3): Acid Extraction Results and Borate Fusion Results for Six Randomly Selected Samples for Cacium concentration versus recovery%.

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الخلاصة

تضمنت هذه الدراسة استخدم مزيج مغلي من حامض الهيدروكلوريك بنسبة 20% و حامض النتريك بنسبة 80% لتقدير العناصر الموجودة كمترسبات في مجرى نهر المحاويل(فرع صغير من نهر دجلة). والعناصر التي تم دراستها هي كل من عنصر الصوديوم ، الكالسيوم ، المغنيسيوم، الكروم، النحاس، الرصاص، الزئبق و النيكل باستخدام تقنية الامتصاص الذري غير اللهبي فكانت نسبة الاسترجاع عالية 96، 97، 99، 99، 97 و 95 لكل من العناصر اعلاه على التوالي مع مدى خطية 100-250 و 80-180 و180- 250 نانوغرام/مل لكل من الرصاص والنيكل والكروم على التوالي وان الانحراف القياسي النسبي أقل من 3%.