Reliability of Grieg Extraction Method for the Determination of Heavy Metals in Aquatic Sediments by Atomic Absorption Spectroscopy

Won Sick Lee and Malcolm L. Sturchio*
Department of Chemistry, College of Education, Seoul National University, Seoul, Korea

ABSTRACT

The extracting efficiency and reliability of the Grieg extraction method for the determination of heavy metals in aquatic sediments were studied by use of an atomic absorption spectroscopy.

The results obtained here reveal clear methodological differences between the Grieg extraction and the HNO_3-$HClO_4$-HF acids extraction method.

The accuracy and precision of the measurements by the Grieg extraction method dec reased on the average in the comparison.

The accuracies of the measurements of trace heavy metals in the sediments—expressed as the double standard deviation $2\sigma(\bar{X})$—were found between about 6% and 17% for the Grieg method, and between about 4% and 15% for the HNO_3-$HClO_4$-HF acids method.

The Grieg extraction method is not a recommendable technique for the determination of trace heavy metals in sediments.

INTRODUCTION

There are a large number of publications dealing with the determination of heavymetals which pollute many surface waters, soils and sediments to a sometimes considerable extent (Hesse, 1971). A large part of the originally dissolved or finely dispersed metals is deposited in the sediments so that a reservior of potentially remobilizable heavy metals

*Department of Chemistry, Fairleigh Dickinson University, New Jersey 07940, U.S.A.

accumulates.

In order to determine metals in sediments by atomic absorption spectroscopy, it is first necessary to bring them into solution. Extraction methods have been well documented and involve fusion or acid dissolution (Lundell, 1938). Five mineral acids (hydrochloric, nitric, sulfuric, perchloric and hydrofluoric acid) have been widely used in geochemcal and soil analysis (Jackson, 1958, Blacik, 1965, Maxwell, 1968). For the simultaneous extraction of a large number of metals, it has been used in conjunction with nitric, hydrochloric and perchloric acid or hydrofluoric acid in the total decomposition of silicates.

Recently, an extraction method by Grieg reagent for determination of heavy metals in sediments applying by some geologists in the United States. The authors have been doubted on reliability of the method. Before a chemical analysis can be employed, we must decide if the aocuracy of the procedure is sufficient for the intended purposes. A qualitative or semiquantitative analysis might be acceptable in some instances, but under other circumstances, only a exact procedure will be able to provide the necessary information (Goode, 1979).

The intention of this study is to decide the reliability of the Grieg extraction method for the determination of trace heavy metals in sediments by atomic absorption spectroscopy.

EXPERIMENTAL

SAMPLE: The sample was taken in the zone of Lower New York Bay. After freezing, all sediment samples were dried in an air bath at 60°C and crushed to a particle size of 80 mesh.

APPARATUS: All determinations were made on a Perkin-Elmer 303 Atomic Absorption Spectrophotometer. An air-acetylene burner and Westing-House Hollow Cathode Lamps were used for all determinations.

REAGENTS:

Grieg extraction reagent: (1) + (2) + (3)

(1) Grieg solution: 80ml HNO_3 (16N) + 20ml HCl (36N) dilute to 1000ml

(2) NH_4Cl (8%)

(3) $Ca(NO_3)_24H_2O$ 4.7g dilute to 1000ml

Hydrochloric acid HCl (36N)

Nitric acid HNO_3 (16N)

Perchloric acid $HClO_4$(60%)

Hydrofluoric acid HF(48%)

Hydrogenperoxide H_2O_2(30%)

Potassiumpermanganate $KMnO_4$(5%)

Standard solutions: All solutions were prepared by serial dilution of 1000mg/l stock solutions

PROCEDURES:

1. Grieg extraction method
   (1) Weigh 5 grams of dry sed. and put it into a digestion bottle
   (2) Add 10ml of HNO_3
   (3) Add 1ml of H_2O_2
   (4) Heat at low temperature until dry. Watch splattering (takes long time). Let cool to room temperature
   (5) Add 10ml of "Grieg solution"
   (6) Add 10ml of NH_4Cl
   (7) Add 20ml of $Ca(NO_3)_24H_2O$
   (8) Heat for 15 min. Break up sed. with glass rod. Let sit overnight
   (9) Filter. Add $KMnO_4$ solution, and dilute to 100ml
2. Extraction by HNO_3-$HClO_4$-HF acids method
   (1) Weigh 1 gram of dry sed. and put it into a platinum clucible
   (2) Add 4ml of HNO_3
   (3) Add 1ml of $HClO_4$
   (4) Add 6ml of HF
   (5) Heat at low temperature until dry. Watch splattering. Let cool to room temperature
   (6) Dilute to 100ml

Ten samples obtained from the bay sediment (same place) were divided into two groups:

Group 1; Five samples, for the Grieg extraction test

Group 2; Five samples, for the HNO_3-$HClO_4$-HF acids extraction test

Oliver (1973) showed that the size of sediment particles strongly influenced the extractable metal content of the samples. Hawkes and Webb (1962) recommended

that the 80-mesh particle size are suitable for contrasting. Thus, the 80-mesh portion of the sample was analysed in this study.

3. Determination, by atomic absorption spectroscopy
4. Data treatment and measurement of accuracy

RESULTS and DISCUSSION

Tables 1 and 2 show the degree of extraction of several heavy metals (10) by use of the methods under consideration (Table 1 Grieg, Table 2 HNO_3-$HClO_4$-HF). The tables also show the element concentration with corresponding $2\sigma(\bar{X})$-errors computed from Equations (1) and (2) (Ackerman, 1976).

$$\bar{X}=\frac{1}{n}\sum_{i=1}^{n}X_i \qquad (1)$$

$$2\sigma(\bar{X})=2\sqrt{\sum_{i=1}^{n}\frac{(\bar{X}-X_i)^2}{n(n-1)}} \qquad (2)$$

where, X_i : a single concentration value of the element concerned
$\bar{X}$: a mean value of a group of X_i
σ : standard deviation
2σ : double standard deviation
n : number of individual measurements per element

Figure 1 shows the comparison of overall distribution, mean values obtained from the two methods and corresponding $2\sigma(\bar{X})$-errors.

The results given in Tables 1, 2, 3 and Fig. 1 indicate that the Grieg solution extract relatively small fraction of the metals especially Mn, Cr, Ni, Co, Ag and Cd from the sediments. (Compare the Grieg extraction with the HNO_3-$HClO_4$-HF method)

Iron was the predominate metal in the sediment and copper showed the highest efficiency of the extraction.

In the comparison of mean values($\bar{X}$) of four metals (Pb, Zn, Fe, Cu), about 75~95% (high efficiency) of the metals could be extracted by the Grieg extraction from the solutions. And in the comparison of mean values of six metals (Cd, Mn, Ni, Co, Cr, Ag), about 40~60% (low efficiency) of the metals could be extracted by the method. (Table 3)

This information show that the Grieg solution less attack on the crystal lattice of the sediment than the HNO_3-$HClO_4$-HF solution, and thus give lower values. (Tables 1 and 2)

Table 1. Overall distribution of 10 heavy metal elements concentrations obtained as a result of the "Grieg extraction" and corresponding $2\sigma(\bar{X})$-errors computed from Eqs. (1) and (2).

(ppm)

Me	Sample no. (extracted from same sample)						dsd	dsd
	1	2	3	4	5	Mean($\bar{X}$)	$2\sigma(\bar{X})$	$2\sigma(\bar{X})$%
Fe	15160	16430	16940	17870	18510	16982	1162	6.84
Zn	341	378	386	389	406	380	21.53	5.67
Pb	278	319	327	330	351	321	23.96	7.46
Mn	231	242	270	274	283	260	19.95	7.67
Cr	231	238	250	268	268	251	15.15	6.03
Cu	192	194	198	212	224	204	12.20	5.98
Ni	13.8	14.0	16.3	16.8	18.1	15.8	1.66	10.51
Co	9.7	9.8	10.4	11.8	12.3	10.8	1.06	9.81
Ag	6.2	8.0	9.5	9.5	9.8	8.6	1.35	15.76
Cd	3.4	3.8	4.0	5.0	5.3	4.3	0.73	16.98
	low ⟵ ⟶ high					mean		9.27

Table 2. Overall distribution of 10 heavy metal elements concentrations obtained as a result of the "HNO_3-$HClO_4$-HF" extraction and corresponding $2\sigma(\bar{X})$-errors computed from Eqs. (1) and (2).

(ppm)

Me	Sample no. (extracted from same sample)						dsd	dsd
	1	2	3	4	5	Mean($\bar{X}$)	$2\sigma(\bar{X})$	$2\sigma(\bar{X})$%
Fe	18450	18620	19940	20120	21240	19674	1033	5.25
Zn	432	449	469	481	489	464	20.92	4.51
Pb	400	401	428	438	458	425	22.22	5.23
Mn	542	546	562	618	622	578	34.96	6.05
Cr	416	465	470	482	497	466	27.33	5.86
Cu	203	208	213	222	229	215	9.40	4.37
Ni	29.2	29.6	33.0	35.0	35.2	32.4	2.57	7.93
Co	19.2	20.2	21.8	23.0	23.8	21.6	1.71	7.90
Ag	11.6	12.4	13.9	16.2	17.4	14.3	2.20	15.41
Cd	8.8	9.0	11.4	12.0	12.3	10.7	1.50	14.01
	low ⟵ ⟶ high					mean		7.65

Mn : Oxidized by H_2O_2
dsd : Double standard deviation

It is apparent from Table 1 that for the sample studied, the Grieg solution does not liberate all of the metal from the silicate matrix. The amount of metal extracted by the Grieg solution depends on the type of sample.

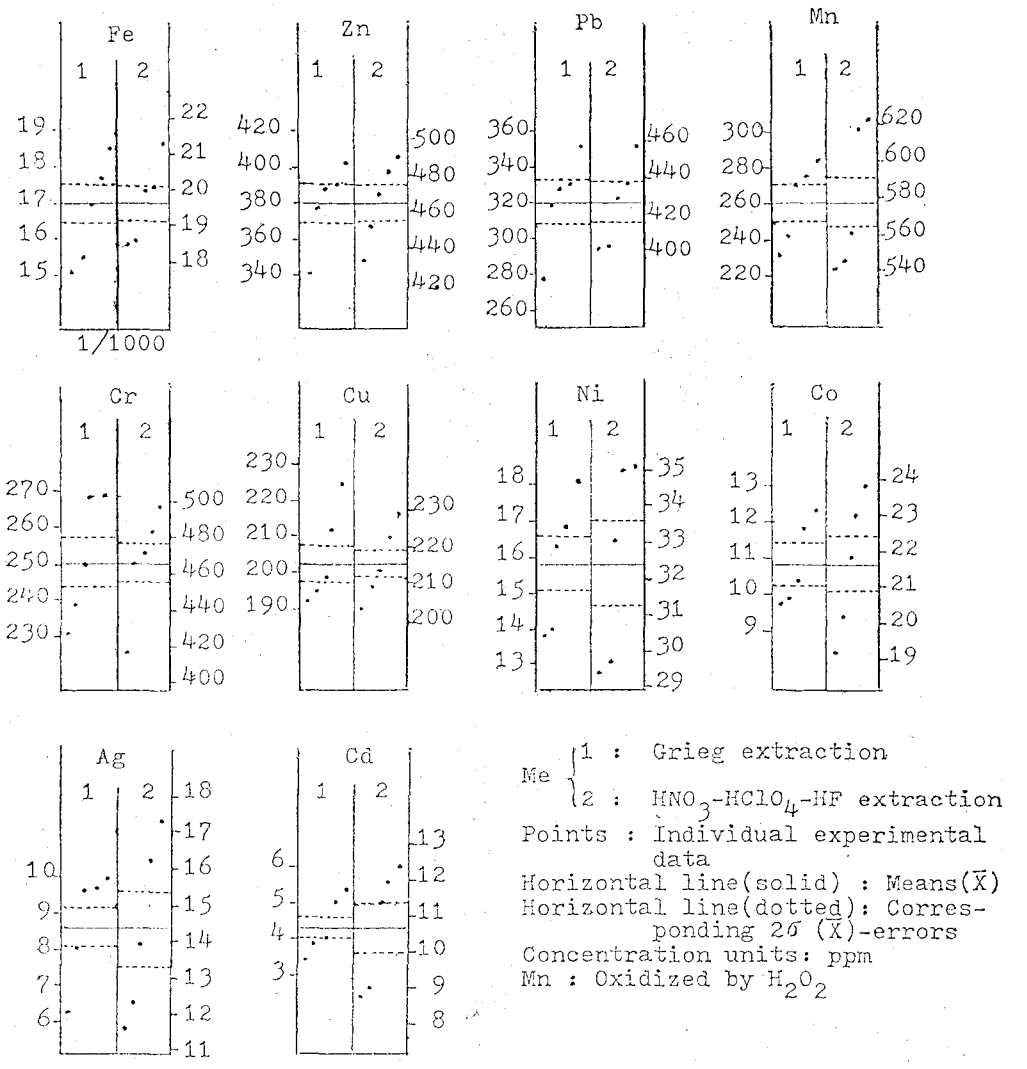

Fig. 1. Comparison of overall distribution of 10 heavy metal elements concentrations obtained as a results of the two methods and corresponding $2\sigma(\bar{X})$-errors.

Holmes, Slade and Mc Lerran (1974) used boiling nitric acid to extract the zinc and cadmium that is bound in organic or sulfide compounds. They extracted about 85% of the zinc and cadmium from some bottom sediments.

Jones (1973) reported extractions of 75% of the zinc and 60% of the cadmium from some bottom sediments.

In consideration of extraction of such elements, the fraction of the total metal extracted

Table 3. Comparison of the mean values and the double standard deviation(%) in the two methods

Me	Mean value($\bar{X}$)				% Double standard deviation			
	Grieg	:	Acids	% of Grieg	Grieg	:	Acids	% of Grieg
Fe	16982	:	19674	86.32	6.84	:	5.25	130.29
Zn	380	:	464	81.90	5.67	:	4.51	125.72
Pb	321	:	425	75.53	7.46	:	5.23	142.64
Mn	260	:	578	44.98	7.67	:	6.05	126.78
Cr	251	:	466	53.86	6.03	:	5.86	102.90
Cu	204	:	215	94.88	5.98	:	4.37	136.84
Ni	15.8	:	32.4	48.77	10.51	:	7.93	132.53
Co	10.8	:	21.6	50.00	9.81	:	7.90	124.18
Ag	8.6	:	14.3	60.14	15.76	:	15.41	102.27
Cd	4.3	:	10.7	40.19	16.90	:	14.01	120.63
Mean					9.27	:	7.65	121.18

by any partial extraction technique will depend on the type of sample used.

Bradshaw, Thomoson, Smee and Larsson (1974) stated that dilute hydrochloric acid may attack some of the less resistant silicates, such as layered silicates.

As was to be expected, the scatter of the majority of each five individual measurement for an element is much larger in the method of Grieg than that of the HNO_3-$HClO_4$-HF extraction. The double standard deviation according to Eq. (2) serves as a measure of these methodological errors and of the accuracy of the mean value of the individual element.

It can be seen that the average accuracy(double standard deviation) of the individual means is between about 6% and 17% for the Grieg method and between about 4% and 15% for the HNO_3-$HClO_4$-HF extraction. (Table 3)

Seven metals(Zn, Cu, Cr, Fe, Pb, Mn, Co) show about 6~10%(low category) and three metals(Ni, Ag, Cd) show about 10~17%(high category) of the average accuracy(dsd) in the Grieg extraction method. (Table 1)

Eight metals(Cu, Zn, Pb, Fe, Cr, Mn, Co, Ni) show about 4~8%(low category) and two metals(Cd, Ag) show about 14~15%(high category) of the average accuracy(dsd) in the HNO_3-$HClO_4$-HF extraction method. (Table 2)

The double standard deviation of measured values obtained with the Grieg method increased in most cases(mean dsd 9.27) and that of the HNO_3-$HClO_4$-HF method decreased markedly(mean dsd 7.65). (Table 3). This means that in intercomparison analysis of the

two mbethods the accuracy of measured values obtained with the Grieg method about 20% decreased than that of the HNO_3-$HClO_4$-HF acids method. (Table 3)

CONCLUSION

The Grieg extraction method should be avoided by replacing the HNO_3-$HClO_4$-HF extraction method for the determination of heavy metals in aquatic sediments by atomic absorption spectroscopy.

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原子吸收分光法으로 水中 沈降物의 重金屬을 定量할 때 사용하는 그리이그 抽出法의 信賴度

李 元 植 · M.L. Sturchio*
(化學敎育科)

要　約

水中 沈降物에 들어있는 重金屬의 原子吸收分光法에 의한 定量에 사용되는 Grieg 抽出法의 抽出效率과 信賴度를 HNO_3-HCl_4-HF 抽出法과 비교하였다. Grieg 抽出法은 HNO_3-$HClO_4$-HF 抽出法에 비하여 抽出效率이 떨어지며, 測定에 있어서의 正確度와 精密度가 일반적으로 낮은 結果를 나타내고 있다.

沈降物에 들어있는 微量 重金屬의 測定에 있어서 正確度(더블標準偏差 $2\sigma(\bar{X})$로 표시된)는 Grieg法에서 약 6%와 17% 사이에, 그리고 HNO_3-$HClO_4$-HF 法에서 약 4%와 15% 사이에 걸쳐있는 것을 알 수 있다. 따라서 Grieg 抽出法은 이 分析法에서 추천할만한 抽出法이 되지 않는다고 볼 수 있다.

* 美國, Fairleigh Dickinson 大學校 化學科