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

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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 HNO₃-HClO₄-HF acids extraction method.

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

The accuracies of the measurements of trace heavy metals in the sediments—expressed as the double standard deviation \(2\sigma(X)\)—were found between about 6% and 17% for the Grieg method, and between about 4% and 15% for the HNO₃-HClO₄-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 heavy metals 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 reservoir of potentially remobilizable heavy metals

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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 geochemical 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 accuracy 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 HNO₃ (16N) + 20ml HCl (36N) dilute to 1000ml
(2) NH₄Cl (8%)
(3) Ca(NO₃)₂₄H₂O 4.7g dilute to 1000ml

Hydrochloric acid HCl (36N)

Nitric acid HNO₃ (16N)
Reliability of Grieg Extraction Method for the Determination of Heavy Metals

Perchloric acid HClO₄(60%)
Hydrofluoric acid HF(48%)
Hydrogenperoxide H₂O₂(30%)
Potassiumpermanganate KMnO₄(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 HNO₃
   (3) Add 1ml of H₂O₂
   (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 NH₄Cl
   (7) Add 20ml of Ca(NO₃)₂·4H₂O
   (8) Heat for 15 min. Break up sed. with glass rod. Let sit overnight
   (9) Filter. Add KMnO₄ solution, and dilute to 100ml

2. Extraction by HNO₃-HClO₄-HF acids method
   (1) Weigh 1 gram of dry sed. and put it into a platinum crucible
   (2) Add 4ml of HNO₃
   (3) Add 1ml of HClO₄
   (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 HNO₃-HClO₄-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 by use of the methods under consideration (Table 1 Grieg, Table 2 HNO$_3$-HCIO$_4$-HF). The tables also show the element concentration with corresponding $2\sigma(\bar{X})$-errors computed from Equations (1) and (2) (Ackerman, 1976).

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

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

where, $X_i$: a single concentration value of the element concerned
$\bar{X}$: a mean value of a group of $X_i$
$\sigma$: standard deviation
$2\sigma$: 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$_3$-HCIO$_4$-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$_3$-HCIO$_4$-HF solution, and thus give lower values. (Tables 1 and 2)
Reliability of Grieg Extraction Method for the Determination of Heavy Metals

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

<table>
<thead>
<tr>
<th>Me</th>
<th>Sample no. (extracted from same sample)</th>
<th>dsd</th>
<th>dsd</th>
<th>Mean($X$)</th>
<th>$2\sigma(X)$</th>
<th>$2\sigma(X)$%</th>
</tr>
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<tr>
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<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
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<tr>
<td>Fe</td>
<td>15160 16430 16940 17870 18510 16982 1162</td>
<td>6.84</td>
<td></td>
<td></td>
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<tr>
<td>Zn</td>
<td>341 378 386 389 406 380 21.53</td>
<td>5.67</td>
<td></td>
<td></td>
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<tr>
<td>Pb</td>
<td>278 319 327 330 351 321 23.96</td>
<td>7.46</td>
<td></td>
<td></td>
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<tr>
<td>Mn</td>
<td>231 242 270 274 283 260 15.95</td>
<td>6.03</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Cr</td>
<td>231 238 250 268 268 251 15.15</td>
<td>6.03</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Cu</td>
<td>192 194 198 212 224 204 12.20</td>
<td>5.98</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>13.8 14.0 16.3 16.8 15.8 15.8 1.66</td>
<td>10.51</td>
<td></td>
<td></td>
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<tr>
<td>Co</td>
<td>9.7 9.8 10.4 11.8 10.8 9.8 1.06</td>
<td>9.81</td>
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<tr>
<td>Ag</td>
<td>6.2 8.0 9.5 9.5 9.8 8.6 1.35</td>
<td>15.76</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Cd</td>
<td>3.4 3.8 4.0 4.0 4.3 4.3 0.73</td>
<td>16.98</td>
<td></td>
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</table>

Table 2. Overall distribution of 10 heavy metal elements concentrations obtained as a result of the "HNO$_3$-HClO$_4$-HF" extraction and corresponding $2\sigma(X)$-errors computed from Eqs. (1) and (2).

<table>
<thead>
<tr>
<th>Me</th>
<th>Sample no. (extracted from same sample)</th>
<th>dsd</th>
<th>dsd</th>
<th>Mean($X$)</th>
<th>$2\sigma(X)$</th>
<th>$2\sigma(X)$%</th>
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<td>4</td>
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<tr>
<td>Fe</td>
<td>18450 18620 19940 20120 21240 19674 1033</td>
<td>5.25</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Zn</td>
<td>432 449 469 481 489 464</td>
<td>20.92</td>
<td>4.51</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Pb</td>
<td>400 401 428 438 458 425</td>
<td>22.22</td>
<td>5.23</td>
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</tr>
<tr>
<td>Mn</td>
<td>542 546 562 618 622 578</td>
<td>34.96</td>
<td>6.05</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Cr</td>
<td>416 465</td>
<td>497 466</td>
<td>27.33</td>
<td>5.86</td>
<td></td>
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</tr>
<tr>
<td>Cu</td>
<td>203 208 213 222 229 215</td>
<td>9.40</td>
<td>4.37</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Ni</td>
<td>29.2 29.6 32.0 35.0 35.2 32.4</td>
<td>2.57</td>
<td>7.93</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>19.2 20.2 21.8 23.0 23.8 21.6</td>
<td>1.71</td>
<td>7.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>11.6 12.4 13.9 16.2 17.4 14.3</td>
<td>2.20</td>
<td>15.41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>8.8 9.0 11.4 12.0 12.3 10.7</td>
<td>1.50</td>
<td>14.01</td>
<td></td>
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</tr>
</tbody>
</table>

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.
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

<table>
<thead>
<tr>
<th>Me</th>
<th>Mean value(%)</th>
<th>% Double standard deviation</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Grieg : Acids</td>
<td>% of Grieg</td>
</tr>
<tr>
<td>Fe</td>
<td>16982 : 19674</td>
<td>86.32</td>
</tr>
<tr>
<td>Zn</td>
<td>380 : 464</td>
<td>81.90</td>
</tr>
<tr>
<td>Pb</td>
<td>321 : 425</td>
<td>75.53</td>
</tr>
<tr>
<td>Mn</td>
<td>260 : 578</td>
<td>44.98</td>
</tr>
<tr>
<td>Cr</td>
<td>251 : 466</td>
<td>53.86</td>
</tr>
<tr>
<td>Cu</td>
<td>204 : 215</td>
<td>94.88</td>
</tr>
<tr>
<td>Ni</td>
<td>15.8 : 32.4</td>
<td>48.77</td>
</tr>
<tr>
<td>Co</td>
<td>10.8 : 21.6</td>
<td>50.00</td>
</tr>
<tr>
<td>Ag</td>
<td>8.6 : 14.3</td>
<td>60.14</td>
</tr>
<tr>
<td>Cd</td>
<td>4.3 : 10.7</td>
<td>40.19</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>9.27 : 7.65</td>
</tr>
</tbody>
</table>

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 HNO₃-HClO₄-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 HNO₃-HClO₄-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 HNO₃-HClO₄-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 HNO₃-HClO₄-HF method decreased markedly (mean dsd 7.65). (Table 3). This means that in intercomparison analysis of the
two methods the accuracy of measured values obtained with the Grieg method about 20% decreased than that of the HNO₃-HClO₄-HF acids method. (Table 3)

CONCLUSION

The Grieg extraction method should be avoided by replacing the HNO₃-HClO₄-HF extraction method for the determination of heavy metals in aquatic sediments by atomic absorption spectroscopy.

ACKNOWLEDGEMENTS

This work was supported by the Grant of the SNU-AID Basic Sciences Program. The authors wish to thank Dr. Nadeau (Dept. of Geology, Ride College, NJ, USA) for his helpful suggestions regarding the studies of the Grieg extraction method.

REFERENCES


原子吸收分光法으로水中沈降物의 重金属を定量할 때 사용하는
Grieg 抽出法の 信頼度

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（化學教育科）

要　約
水中沈降物に含まれる重金属の原子吸光分光法に用いる定量に使用される Grieg 抽出法の抽出効率と信頼度を HNO₃-HCl₄-HF 抽出法と比較した。Grieg 抽出法は HNO₃-
HCl₄-HF 抽出法に比べ抽出効率が劣り、測定にあたっての正確度と精密度が若干低くなる結果を示し得ている。
沈降物に含まれる微量重金属の測定において正確度（測定標準偏差 2σ(X)を示す）
は Grieg法では約 6%と 17% 以下で、そして HNO₃-HCl₄-HF 法で約 4%と15% 以下に近くなることが示された。こ
の抽出法はこの分析法において抽出法が不完全であることを示す。