Bull. Environ. Contam. Toxicol. (1998) 60:425-432

Bulletin of Environmental Contamination and Toxicology

Comparison of Digestion Techniques in Analyses for Total Metals in Marine Sediments

D. L. Trimm,[1] H. H. Beiro,[2] S. J. Parker[2]

[1]EnSafe, 2114 Airport Boulevard, Suite 1150, Pensacola, Florida 32504, USA
[2]EnSafe, c/o CMES, Post Office Box 489, 209 Wallace Avenue, Kevil, Kentucky 42053-0489, USA

Received: 10 August 1997/Accepted: 24 December 1997

It is generally recognized that in order to achieve a complete dissolution all metals within a sediment, some combination of hydrofluoric acid (HF) with other acids is required to release all metals from their silicate structures. This is because silicates are resistant to most mineral acids. Previous studies by Loring and Rantala (1988) assessed laboratory variability in determining total metal concentrations using hydrofluoric acid (HF) and nitric acid (NA) dissolution and extraction procedures. Studies on trace metal concentrations in estuarine and coastal marine sediments from the southeast US, and Florida in particular, recognized the need for a HF digestion (Windom et al. 1989). Schropp et al. (1990) used a HF digestion method to determine 'natural' metal-to-aluminum relationships for Florida sediments.

To meet the requirements of the federal Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), USEPA has established the Contract Laboratory Program (CLP) as an analytical standard. This method employs a NA digestion for estuarine and marine sediment metals analysis. However, since digestion method techniques under the CLP program are different than those used by Schropp et al. (1990), a comparison of the methods was in order. The results of this comparison could allow using the regression lines provided by FDER (1988) or Schropp et al. (1990) on sediments analyzed under the CLP for CERCLA. The overall study objective was to determine if metal data analyzed by a CLP NA digestion was comparable to metal data produced by using a HF digestion method.

MATERIALS AND METHODS

Twenty-nine locations within Pensacola Bay and Bayou Grande, Florida, were randomly selected for a

---

Correspondence to: D. L. Trimm

comparative sediment digestion analysis. These sampling locations were examined after selection to ensure a variety of bottom types. This was done to prevent one bottom type from dominating the study. From December 1995 to February 1996, sediment samples were collected using a stainless-steel Ekman grab (529 cm^2). Two grab samples were collected from the top 5 to 6-cm and placed in a stainless-steel mixing bowl for compositing. From this composite sample, pre-cleaned containers were filled for immediate shipment to the laboratory. Samples were stored and shipped on ice within 24 hrs by a priority delivery service.

Each of the 29 samples were divided by the lab into two aliquots to be analyzed by inductively coupled plasma (ICP) emission spectroscopy. One aliquot would be digested in accordance with the standard procedure using NA, while the other would utilize a 50:50 mixture of HF and NA (1:1). Both digestion methods use 1 g (wet weight ± 0.50 g) of sediment weighed into an acid-washed Teflon beaker. Under the CLP NA digestion, the sample is allowed to reflux at 95°C with 10 mL of 1:l nitric acid for 10 minutes without boiling. The digestate was then allowed to cool and 30% hydrogen peroxide added in 1 mL aliquots until no further vigorous effervesce was noted. No more than 10 mL of hydrogen peroxide was added at any time. Since these samples were to be analyzed by ICP, hydrochloric acid was added to the final acid-peroxide digestate. Insoluble materials were then filtered through a Whatman no.42 filter and brought to 100 mL volume by adding ASTM Type II water.

The method was modified to include the HF by using 5 mL of HF and 5 mL of NA (1:1) allowing the mixture to sit at room temperature for eight to twelve hrs. Next gentle heat (~ 70° C) was applied and the samples were allowed to reflux for eight to twelve hrs. The higher temperatures used in the CLP procedure would cause the HF mixture to boil. It was believed that boiling the acid mixture may affect the study results. At the end of this period another 5 mL of each acid was added to the samples. The samples were again refluxed for eight to twelve hrs at ~ 70°C. As before, hydrochloric acid was added to the digestate, filtered, and brought to 100 mL volume by adding ASTM Type II water.
Both types of digestates were analyzed for total metals in accordance with the CLP inorganic statement of work ILM03.0 for ICP. To meet the requirements of this study, trace ICP emission spectroscopy was used to

provide low level analysis modifying the interference check sample to include low level arsenic and lead.

The individual metal analytical results were first tested for relationships between the two digestion procedures. To illustrate the relationship between the HF and NA digestates, scatter plots were produced. Each ordered pair (x,y) representing x = NA and y = HF was plotted as a point; the similarity between the different digestion methods is illustrated by their closeness to the x = y line. If x is greater than y, most of the data will fall below the line. When y exceeds x, the data will lie largely above the x = y line.

To test whether the HF digestion tended to produce overall larger values than those produced by NA digestion, the Mann-Whitney rank-sum test was employed (Helsel and Hirsh, 1995). This non-parametric procedure can assess whether two independent groups differ. This non-parametric approach was used rather than a parametric t-test based on the results of normality testing. Although these distributions could be transformed to approach normality, justification for the use of a non-parametric versus a parametric test was based on discussions by Blair and Higgins (1980). They found that small deviations from a normal distribution were not always detectable in normality tests on small data sets, and that the use of non-parametric methods, such as the Mann-Whitney rank-sum test, exhibited large advantages in power over the t-test.

Finally, data produced by both digestion methods were plotted on regression lines found in FDER (1988) to evaluate where each digestion distribution for each metal occurred relative to the Schropp et al. (1990) and FDER (1988) regression lines for 'clean' sediments. It was hoped that differences in the digestion methods might be clarified so that past and future CLP NA data could be assessed with these regressions.

RESULTS AND DISCUSSION

Table 1 provides a comparison of descriptive statistics produced from the two digestion procedures. Comparing the mean and median results for HF to CLP NA digestion revealed no apparent differences with the exception of nickel. The distributions are likely not normal suggested by the high standard deviations. Based on the

Mann-Whitney Test, no statistical significant difference was found between the two data sets.

Table 1. Descriptive Statistics for HF and NA Metals Digestion Methods

	N	Mean (mg/kg)	Median (mg/kg)	St. Dev.	SE Mean	Mann-Whitney[a] Results
HF-Al	29	11,869	3,640	15,836	2,941	+
NA-Al	29	8,134	3,490	10,448	1,940	
HF-As	29	5.63	2.20	6.52	1.21	+
NA-As	29	6.18	3.20	7.08	1.32	
HF-Cd	29	1.15	0.46	1.15	0.21	+
NA-Cd	29	1.03	0.45	1.03	0.19	
HF-Cr	29	54.4	13.3	72.1	13.4	+
NA-Cr	29	47.8	10.4	62.5	11.6	
HF-Cu	29	13.11	6.6	15.23	2.83	+
NA-Cu	29	11.59	6.8	12.90	2.40	
HF-Pb	29	34.73	20.8	42.64	7.92	+
NA-Pb	29	36.73	16.3	43.14	8.01	
HF-Ni	29	9.27	2.7	16.6	3.09	+
NA-Ni	29	4.46	2.6	4.9	0.91	
HF-Zn	29	54.7	18.9	66.0	12.3	+
NA-Zn	29	48.9	28.6	55.8	10.4	

NOTE:

[a] No significant difference ($\alpha=0.05$) between method results indicated by +.

St.Dev. = standard deviation

SE = standard error

Scatter plots provided in Figure 1 exhibit a comparison of the two methods relative to increasing metal content. A general observation should be noted that metal content appears to be directly proportional to the variability observed. The data suggests nickel is more effectively dissolved at greater concentrations by the HF digestion method. It has been suggested that this may be due to nickel remaining bound to the matrix during the NA digestion. Cadmium also exhibited extreme variability as concentrations increased. The symmetrical nature of cadmium's scatter plot (Figure 1) suggests the precision of the method may be the problem

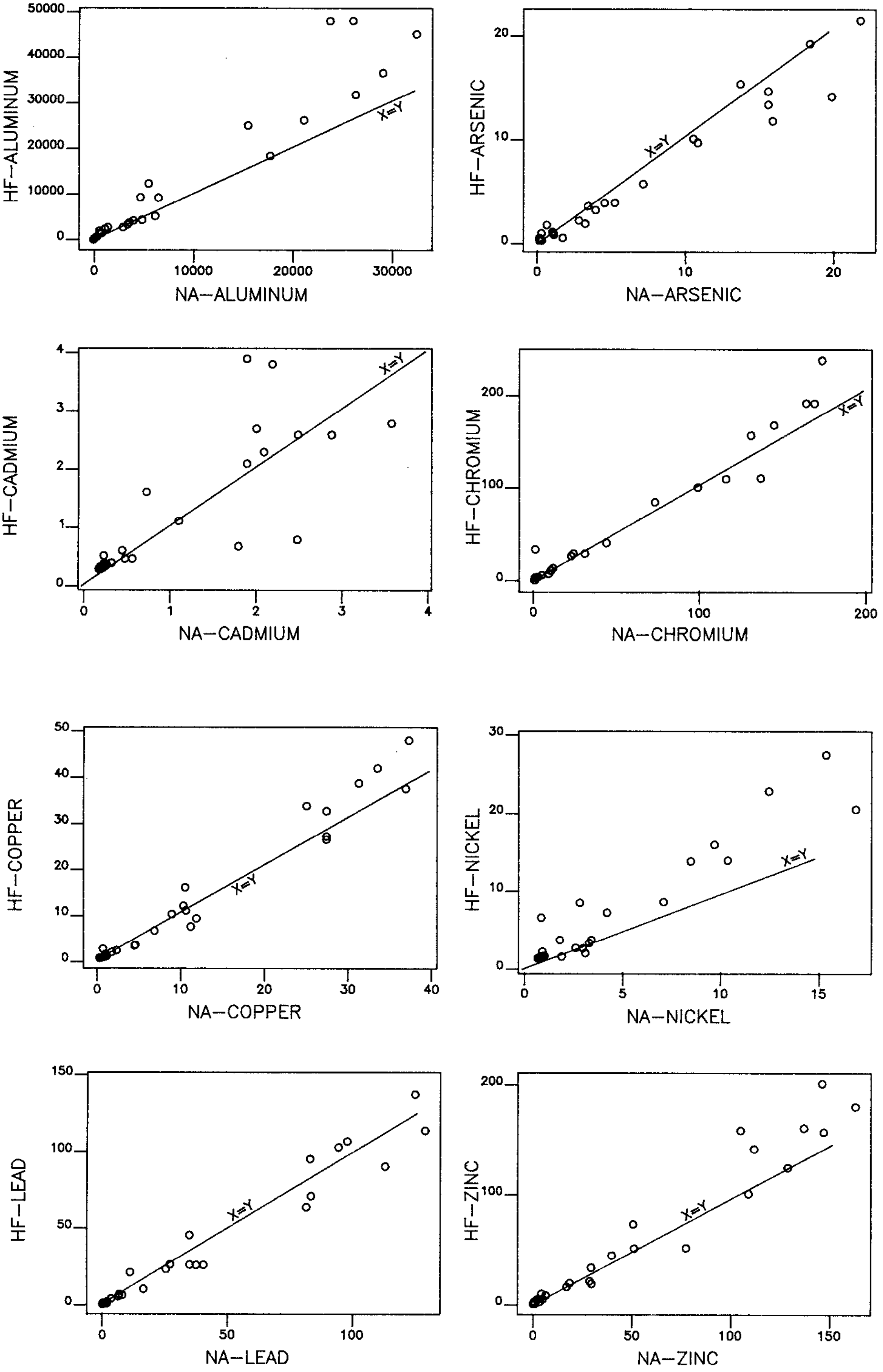

Figure 1. Metal concentrations (mg/Kg) from nitric (NA) and hydrofluoric (HF) digestion methods.

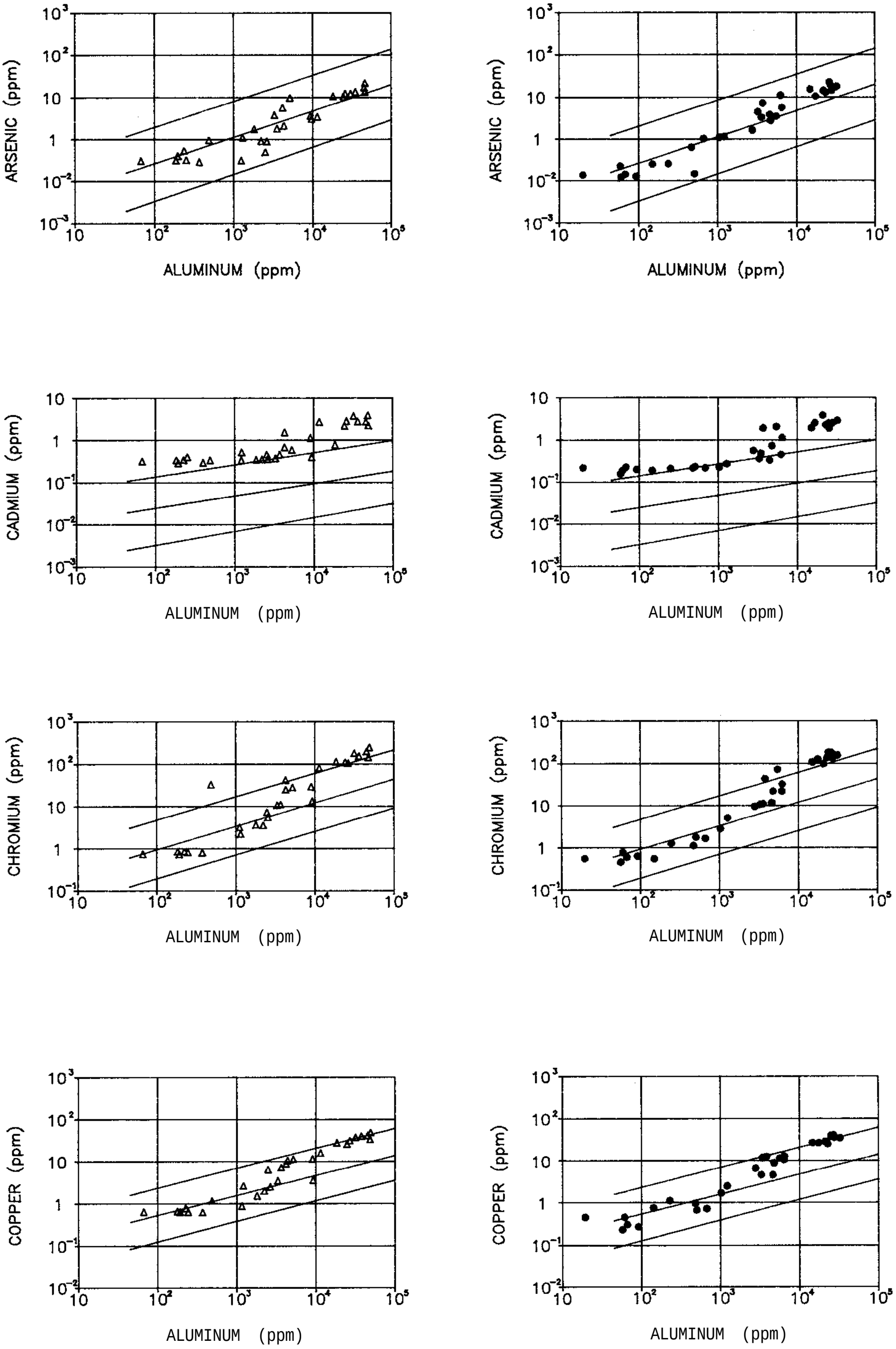

Figure 2 Nitric (NA) and hydrofluoric acid (HF) digestion results plotted on Florida (FDER, 1988) regression lines.

● = NITRIC ACID
Δ = HYDROFLUORIC ACID

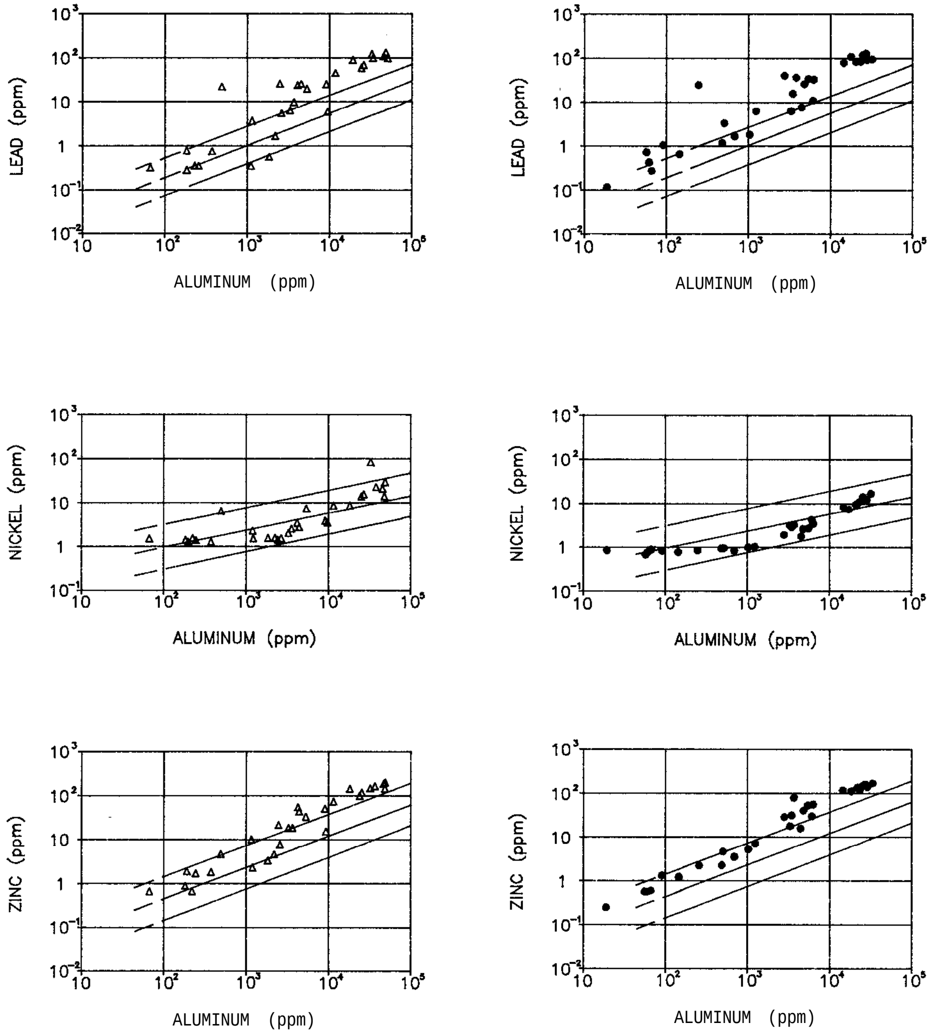

Figure 2. Nitric (NA) and hydrofluoric acid (HF) digestion results (cont.) plotted on Florida (FDER, 1988) regression lines.

● = NITRIC ACID
Δ = HYDROFLUORIC ACID

and is not a function of the digestion technique used. The primary differences between the digestion methods were the HF addition, the length of reflux time, and the digestion temperature. Despite these differences, the aggressive HF digestion did not produce a significant difference in metals being dissolved for analysis.

The two data sets plotted on the FDER (1988) regression lines suggests that individual HF results appear higher than those produced by NA (Figure 2). This is likely due to the longer digestion time and aggressive nature of HF. Each metal has its own character of course, some metals appear identical. These findings suggest that ratios produced by the two methods are comparable. The data produced by NA methods conservatively predict anthropogenic metal contamination on the FDER (1988)regression lines.

Acknowledgments. Funding for this project was provided by Southern Division Naval Facilities Engineering Command. Special thanks to Messrs. Bill Gates and Bill Hill for their support of this study and to Dr. Steven Schropp for his technical input.

REFERENCES

Blair RC, Higgins JJ (1980) A comparison of the power of Wilcoxin's rank-sum statistic to that of student's t statistic under various nonnormal distributions. J Educ Statistics 5:309-335

FDER (1988) A guide to the interpretation of metal concentrations in estuarine sediments. Florida Dept Envir Reg, Coastal Zone Mgmt Sect, p 44

Helsel DR, Hirsch RM (1995) Statistical methods in water resources. Elsevier Science Publ, New York, NY, p 529

Loring DH, Rantala RTT (1988) An intercalibration exercise for trace metals in marine sediments. Mar Chem 24: 13-28

Schropp SJ, Lewis FG, Windom HL, Ryan JD, Calder FD, Burney LC (1990) Interpretation of metal concentrations in estuarine sediments of Florida using aluminum as a reference element. Estuaries 13: 227-235

Windom HL., Schropp SJ, Calder FD, Ryan JD, Smith RG, Burney Jr LC, Lewis FG, Rawlinson CH (1989) Natural trace metal concentrations in estuarine and coastal marine sediments of the southeastern United States. Environ Sci Tech 23:314-320