# FINAL REPORT ON THE QUALITY CONTROL
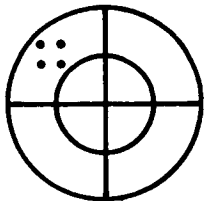# OF TRACE METAL ANALYSIS
# FOR THE MAFLA BASELINE ENVIRONMENTAL SURVEY

AUGUST 1, 1975
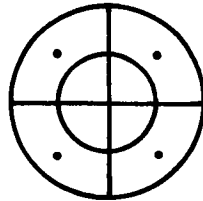
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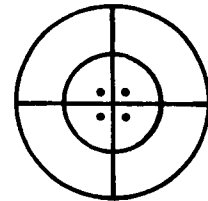
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## DEPARTMENT OF ANALYTICAL CHEMISTRY

August 1, 1975

FINAL REPORT

THE QUALITY CONTROL OF TRACE METAL ANALYSIS FOR THE MAFLA ENVIRONMENTAL SURVEY

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# EXECUTIVE SUMMARY

A comprehensive quality control program was conducted by Gulf
South Research Institute in support of the MAFLA Trace Metal Phase
of the Baseline Environmental Survey for the Bureau of Land Management,
Contract No. 08550-CT4-15 (MAFLA II). Five different types of
marine environmental samples, chosen at random from the samples
analyzed by the prime contractor, were submitted for quality control
verification of eight different trace metals. The classes of marine
environmental samples analyzed included: surficial bottom sediments;
dissolved and suspended metals in the water column; and two aquatic
organisms important in the biological food web, zooplankton and benthic
invertebrates. Raw sediments and filtered waters were submitted for
quality control analysis whereas acid extracts of suspended metals and
biota were obtained. Thirty-five sediments, 15 filtered water, 15
suspended particulate matter, 15 zooplankton, and 20 benthic
invertebrates were subjected to quality control trace metal analysis.
All MAFLA samples were analyzed for the eight trace elements included
in the quality control program: barium, cadmium, lead, vanadium,
nickel, copper, chromium, and iron. All samples were analyzed by flame
and/or flameless atomic absorption spectrophotometry (AAS).

In lieu of available environmental standard reference materials
(SRM) as an aid in obtaining meaningful measurements, in-house SRM's
were prepared as deemed necessary. Trace metal levels in two in-house
sediment SRM's were obtained via exhaustive AAS analysis. The SRM's

were analyzed against both aqueous standards and matrix-matched

standards, since a matrix effect was observed.

The initial sediment standardization experiments were described

in Progress Report I. The results of supplementary quality control

experiments performed with the standard sediments following

publication of Progress Report I are described in this report.

These experiments include additional replicate analyses of the

standard sediments for cadmium, copper, chromium, nickel, and lead

by direct comparison to aqueous standards and vanadium and barium

determinations performed by the method of Standard Additions.

The results of the average matrix determination for composites

prepared from the MAFLA sediment samples are presented for both

major and trace constituents.

The metals present in greatest quantity in the MAFLA sediments

and which dissolve along with trace metals in digesting the samples

included (%, dry wt. basis): calcium (20%); magnesium (3%); iron

(0.7%); aluminum (0.5%); sodium (0.5%), and potassium 0.15%.

The average values of trace metal content found in the composites

were 15 ppm chromium, 6 ppm lead, 3 ppm copper, 6 ppm nickel, 15 ppm

vanadium, and 20 ppm barium.

Each of the MAFLA sediments was analyzed in duplicate for all

eight trace metals*. Barium concentrations averaged 22.7 ppm and

ranged from a low of 4.6 ppm (38)† to a high of 51.1 ppm (3) excluding

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* Results reported in ppm, dry weight basis.
† Numbers and/or letters in parenthesis indicate BLM sample identi-
    fication numbers.

sample 2 (USGS Standard Rock). Vanadium concentrations are reported compared to both aqueous and matrix-matched standards. The average vanadium concentration was 11.4 ppm (against aqueous calibration) versus 9.4 ppm (against matrix-matched calibration); individual sample values ranged from 1.1 ppm (30) to 102 ppm (54). The cadmium content was very low; average, low and high measurements are 0.086 ppm, 0.02 ppm (1), and 0.28 ppm (5) respectively. The lead determination provided equivalent data for aqueous and matrix-matched standards. An average value of 4.7 ppm lead was measured; values of individual samples ranged from 1.7 ppm (7) to 13.4 ppm (26). Nickel content averaged 6.1 ppm when compared to aqueous standards and 6.9 ppm for matrix-matched standards; the samples ranged from a low of 0.3 ppm (24) to a high of 45.7 ppm (2, USGS Standard Rock). The average copper content in the sediments was 1.8 ppm (aqueous) and 2.1 ppm (matrix-matched). One sample (54) was unusually high in copper, 132.2 ppm and unrepresentative of the group of sediments. The remaining 34 samples ranged from a low of 0.2 ppm (38) to a high of 9.0 ppm (26). The chromium measurements averaged 15.4 ppm for aqueous standard comparison versus 12.9 ppm for matrix-matched standard calibration. The low and high chromium measurements were 2.1 ppm (30) and 54.0 ppm (26), respectively. Iron was present in greater than trace quantities in all 35 MAFLA sediment samples. The average (4,877 ppm) and standard deviation (4,614 ppm) were similar; values ranged from a low of 470 ppm (30) to 18,280 ppm (54)

for the individual sample measurements. Quality control provided
for analysis of the MAFLA sediments is described in detail and data
supporting the accuracy of the determinations is presented. The
percent recovery of spiked SRM samples was lowest for the metals
analyzed by flameless AAS techniques (cadmium, 76.4%; barium, 50.8%).
Excellent recoveries were obtained for lead (96.2%), copper (95.7%),
chromium (99.7%), vanadium (99.9%), and nickel (100.5%).

Dissolved and suspended metals in the water column were determined
for seawater samples. The dissolved barium, vanadium, chromium, and
iron content was measured by flameless AAS for the seawater samples.
Nickel, lead, copper, and cadmium was extracted from seawater with
APDC-MIBK and analyzed by flame AAS. The quantity of dissolved iron
ranged from a low of 35 ppb (TM-527) to a high of 425 ppb (TM-921) with
a mean of 159 ppb. The barium content averaged 44 ppb and varied from
11 ppb (TM-920) to 80 ppb (TM-925). Vanadium content ranged from 11.2
ppb (TM-921) to 29.3ppb (TM-535) with a mean value of 19 ppb. The
level of cadmium present in the majority of the seawater samples was
$\leq$ 0.03 ppb (D.L.). Only two samples contained cadmium in detectable
amounts (> 0.03ppb); TM-889 contained 0.09 ppb and TM-922, 0.06 ppb.
Only two samples contained lead in detectable amounts (> 0.2 ppb);
TM-889 and TM-922 contained 2.09 ppb and 34.6 ppb of lead, respectively.
The mean concentration of dissolved nickel measured was 0.74 ppb; values
ranged from 0.2 ppb (TM-363) to 2.77 ppb (TM-880). The copper content
ranged from 0.32 ppb (TM-925) to 8.62 ppb (TM-909) with a mean value
of 2.61 ppb. The range of dissolved chromium varied from 2 ppb (TM-527)
to 6 ppb (TM-880) and averaged 3.4 ppb.

The suspended metals were determined by flameless AAS for ten milliliter acid extracts of the suspended particulate matter prepared by the prime contractor. Nickel and iron were present in the largest quantity averaging 153 ppb and 100 ppb, respectively. The range of nickel was quite variable being 7 ppb (PAD-87) to 600 ppb (PAD-76), while iron varied from 12 ppb (PAD-77) to 284 ppb (PAD-14). Barium was not detected in one sample (PAD-85); the mean barium concentration was 9.5 ppb ranging from a low of 3 ppb (PAD-36) to a high of 26 ppb (PAD-87). The detection limit for vanadium was 5 ppb; none of the samples contained measurable quantities of this element. Cadmium content was quite low and varied from 0.25 ppb (PAD-67 and -77) to 2.20 ppb (PAD-7) and averaged 0.73 ppb for the group of 15 samples. The amount of chromium found was also small averaging 0.58 ppb and ranging from 0.29 ppb (PAD-87) to 1.03 ppb (PAD 7). Lead content averaged 4.9 ppb and varied from 1 ppb (PAD-61) to 20 ppb (PAD-7). The amount of copper was in the same general concentration range (13 ppb to 30 ppb) for all but one sample; PAD-11 contained 62.5 ppb copper compared to a group mean of 23 ppb.

Ten-milliliter extracts of MAFLA benthic invertebrate samples and zooplankton were analyzed. Iron was present in the greatest quantity in extracts of both aquatic organisms; an average of 15,150 ppb with variation from 1,540 ppb (6-5-III-F) to 60,690 ppb (21-I) within the set was measured for benthic invertebrates while zooplankton iron content averaged 4140 ppb and varied from a low of 415 ppb (2) to a high of 21,800 ppb (16). Comparatively large amounts of vanadium

and nickel were found in the benthic invertebrate extracts. Vanadium

content ranged from 140 ppb (6-19-II-B-4) to 2,740 ppb (32-A) with

a mean of 1,650 ppb while nickel content averaged 2,260 ppb and

ranged from 50 ppb (3 samples) to 24,800 ppb (62-B). Copper and

barium content averaged 230 ppb and 262 ppb respectively while

variation within the sample set were 50 ppb (6-18-II-K-1) to

1,300 ppb (21-I) for copper and 40 ppb (51-A) to 580 ppb (21-I)

for barium. Cadmium concentrations in the benthic invertebrate

extracts were either very low (5 ppb to 80 ppb) or very high

(200 ppb to 790 ppb) with a set average of 179 ppb. Lead and

chromium content demonstrated a similar variability with low

lead concentrations in the range of 2 ppb (6-5-III-F) to 15.2 ppb

and higher levels from 20 ppb to 87 ppb (49-A) with a set average

of 23 ppb. A low range of 6 ppb (6-19-II-B-4) to 50 ppb and

higher levels from 100 ppb to 227 ppb (62-B) with a set average

of 82 ppb was observed for chromium.

The concentration of barium in zooplankton extracts ranged from

70 ppb (ZP-2) to 1,490 ppb (ZP-16) with an average of 607 ppb. Nickel

and copper were present in comparable quantities averaging 178 ppb

and 224 ppb with ranges of 50 ppb (ZP-24) to 320 ppb (ZP-16) and 120 ppb

(ZP-25) to 610 ppb (ZP-16) respectively. Cadmium concentration in

the extracts varied from a low 7 ppb (ZP-2) to a high of 350 ppb

(ZP-9) with a mean of 88 ppb. The concentration of vanadium in the

zooplankton extracts averaged 48 ppb and ranged from 13.5 ppb (ZP-3)

to 126.5 ppb (ZP-16). Chromium content was comparatively high for

two samples (ZP-9) and (ZP-16); the mean for the set was 21.2 ppb and the individual samples ranged from 6.4 ppb (ZP-14) to 89 ppb (ZP-16). Lead values were similar within the group ranging from 3.6 ppb (ZP-25) to 11.9 ppb (ZP-9) with a mean of 8.0 ppb lead.

CHAPTER I


INTRODUCTION


The quality control program initiated prior to analysis of the

actual sediment samples collected from the MAFLA Outer Continental

Shelf area was described in BLM Progress Report I (1). Originally

it was thought that a sufficient quantity of each sediment sample

would be supplied by BLM for quality control experiments to be

conducted on the actual project sediments. However, only ten

grams of each of the first 35 samples were provided. Assuming a

four gram sample size (the amount considered minimum at GSRI for

acceptably low AAS detection limits) the maximum number of

determinations per sample would be two. Therefore, it was not possible

to analyze duplicate spiked and duplicate unspiked samples for each

sediment nor could an alternate procedure, such as the Method of

Standard Additions, be employed.

The most reliable solution to accuracy problems is to analyze a

sediment sample of known metal content with each set of unknown

samples. The Environmental Protection Agency (EPA) provides standard

samples for quality control purposes for many different types of

samples and numerous parameters. Unfortunately, a standard sediment

sample is not yet available from EPA or the National Bureau of

Standards although the EPA is in the process of developing such a

standard sample.

It was decided that the next best approach would be to determine average values for the eight metals of interest in the BLM program in standard samples prepared by GSRI. Two large sediment samples were obtained for this purpose: one sample projected to contain low levels of certain metals (Sample A) and one sample with higher expected metal concentrations (Sample B). The sediments were collected from the Pearl River bottom on the Louisiana – Mississippi border (Sample A) and from the bottom of the drainage ditch located at the NASA National Space Technology Laboratories in Bay St. Louis, Mississippi.

The sediment samples were analyzed for barium, vanadium, cadmium, lead, nickel, copper, chromium, and iron in order to obtain accurate concentrations of each metal for eventual use as standard reference materials (SRM). The federally recommended procedures were followed for routine sample preparation and Atomic Absorption Spectrophotometric (AAS) analysis by flame techniques. Analysis of each metal in both samples was also performed by the Method of Standard Additions for comparison purposes. An investigation of AAS interferences suspected of producing erroneous metal concentration values was conducted. The two interferents positively identified were iron and aluminum, both of which were shown to be present in excessive quantities. The effect of these interferents on the accurate determination of the concentration of barium, vanadium, cadmium, lead, nickel, copper, and chromium was examined. Cadmium and lead measurements were the only determinations found to be relatively free of serious interferences when analyzed by flame AAS.

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Later replicate digestions of these two standard sediments were
prepared to add to the information presented in Progress Report I (1).
Cadmium, lead, nickel, copper, and chromium were measured in Sediments
A and B for these new replicate digestions. The same digestions were
used for Standard Additions experiments similar to those reported
earlier (1). Barium and vanadium were analyzed several times by the
Method of Standard Additions. The barium analysis was performed in
order to provide further confirmation of the barium analysis obtained
after addition of potassium and aluminum and iron interferents.
The same methodology was employed for vanadium measurements with
the Standard Additions technique maintaining minimal analyte to
interferent ratio variance (3 to 5%).

The analysis procedure suggested by GSRI for trace metal assay
of the MAFLA samples was tested for the two standard sediments.
Replicate determinations were made of each metal by calibrating the
Atomic Absorption Spectrophotometer with both aqueous standards and
standards containing the quantitities of iron and aluminum interferents
present in the acid digests of the standard sediment samples.

The variation in trace metal content of the standard sediments
as measured against aqueous standards versus matrix-matched standards
demonstrated the need to do a preliminary matrix determination of the
MAFLA sediment samples. The amount of sediment received (10 grams)
precluded a detailed examination of the matrix of each sediment.
An alternative method was used for matrix analysis of the MAFLA samples.

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Several different composite samples were made using a one-gram aliquot of each of the 35 samples. A second set of composites was generated using a one-half-gram aliquot of each sample and different groupings. The results of this matrix examination are presented in Chapter IV, part B, of this report.

The standard sediments, A and B, were used as the standard reference materials (SRM) for quality control purposes following the initial determinations of trace metal content in the SRM's. The details of quality control employed in trace metal analysis of the MAFLA sediments are presented in the Quality Control Section.

The rigorous quality control program developed for trace metal analysis of sediments could not be applied to the analyses of seawater and aquatic organisms due to the form and amount of sample received.

The quantity of seawater received for analysis of dissolved metal was 400 milliliters; extraction of dissolved metals from seawater requires approximately 1500 milliliters of sample for the determination of 8 metals. To overcome this difficulty the trace metal analysis of seawater was performed by flameless atomic absorption spectroscopy. This method provided accurate results for only four of the metals of interest: barium, vanadium, chromium, and iron. The remaining four trace metals were either too volatile or covolatilized with the matrix resulting in irreproducibility of measurements. The remaining quantity of seawater ( ∿375 ml) was extracted with APDC-MIBK and cadmium, lead, nickel, and copper content measured by flame AAS.

The suspended metals in seawater are measured by determining the trace metal content of suspended particulate matter obtained by filtering large volumes of water. The amount of water filtered was not given to GSRI for the 15 suspended particulate matter samples. These samples were received in the form of prepared acid-extracts. The volume supplied (15 ml) was insufficient for analysis by flame AAS. Therefore, these extracts were analyzed for barium, vanadium, cadmium, lead, nickel, copper, chromium, and iron by the flameless graphite furnace technique.

The aquatic organisms analyzed for the MAFLA baseline survey included benthic invertebrates (20 samples) and zooplankton (15 samples). These samples were also received as 10-milliliter acid-extracts prepared by the prime contractor. It was necessary, therefore, to analyze these 35 samples by the flameless graphite furnace atomic absorption method.

The quality control for samples obtained in insufficient quantitites included replicate flameless AAS analyses and a large number of calibration standards.

# CHAPTER II

## EXPERIMENTAL

### A. ATOMIC ABSORPTION SPECTROPHOTOMETRIC INTERFERENCE INVESTIGATION

The trace metal assay of two sediment samples, designated A and B, for eventual use as standard sediments was described in Progress Report I (1). During the process of sediment standardization, inter-ferences resulting from aluminum and iron content were noted. Matrix interferences were discussed in detail and appropriate literature was cited for purposes of documentation (2-29). Additional experiments performed with these sediments will be presented here. Barium was excluded (Figure 1) since flameless AAS was employed for barium analysis of the MAFLA sediments.

### 1. Replicate Analysis of Sediments A and B

The EPA recommended (unofficial) procedure for digestion of sediments for trace metal analysis was used to prepare ten replicate acid extracts of sediment A and sediment B (Appendix A). Four grams of sediment that had been dried to constant weight was used for the digestion and the final dilution volume was 50 milliliters. Atomic Absorption Spectrophotometric analysis was performed for each element with a Perkin-Elmer Model 306 AA unit equipped with a Deuterium Arc Background Corrector. Instrumental parameters estab-lished for use with a particular element have been extended and will

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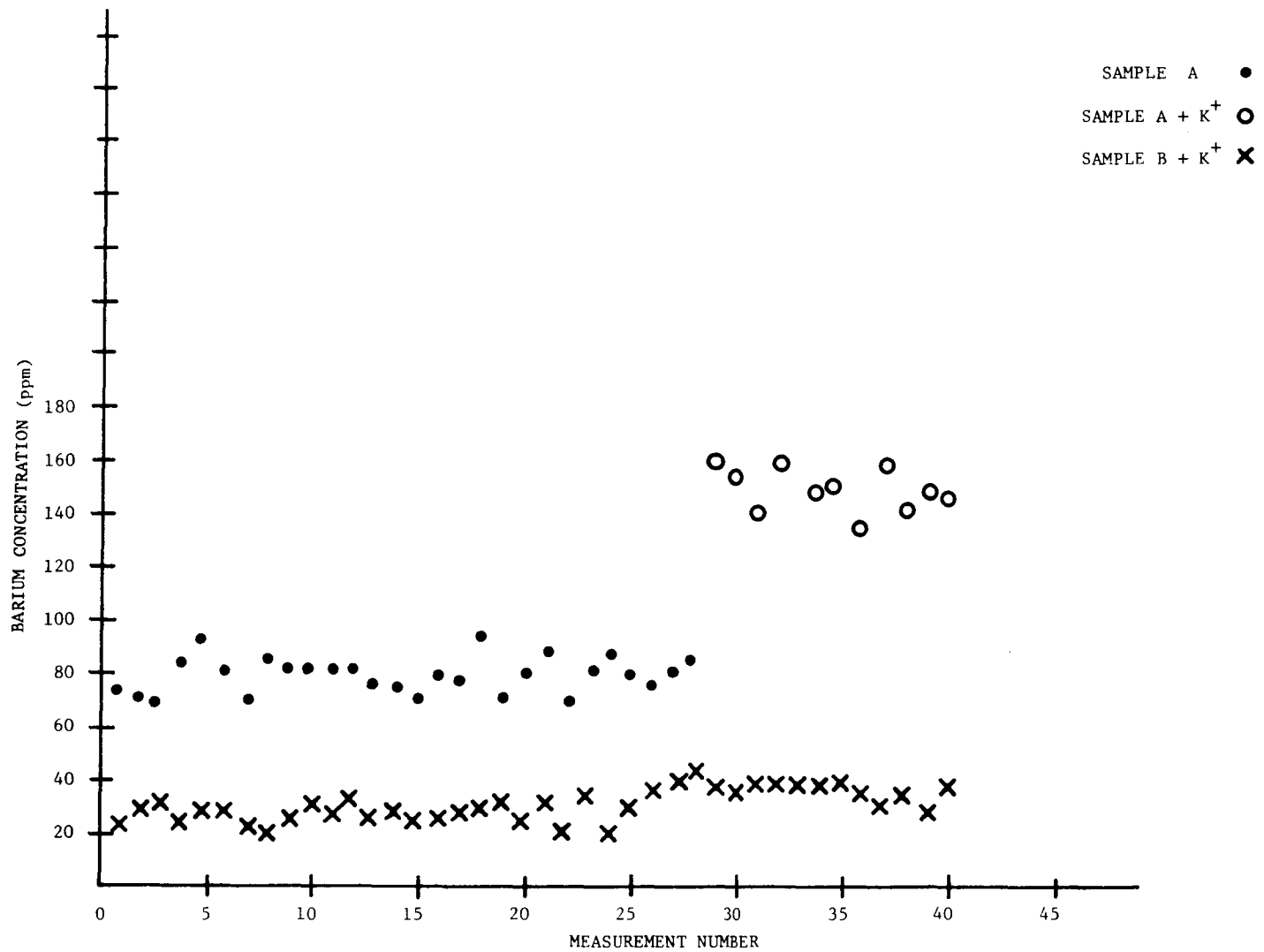
Figure 1. Replicate Analysis of SRM A and B for Barium by Flame AAS.  Acid extracts of the sediments were analyzed with and without added $K^+$ ion as ionization suppressor; results presented on dry weight basis and calculated by direct comparison to aqueous standards.

be described as needed. Burner and Flow Meter settings are in arbitrary units for aid in reproducing instrumental conditions. These parameters apply only to the PE 306 AA in the GSRI laboratory. Therefore wavelengths are those experimentally determined for this monochromator as opposed to the theoretical listing. Each determination was made according to the manufacturer's suggestions except where deemed inappropriate. All pertinent improvements in analysis procedures adopted for the purpose of obtaining accurate assay results will be noted when applicable to a particular measurement.

1. Vanadium

| | |
|---|---|
| H.C. Lamp Current: | 40 ma |
| Slit Width (4): | 1.0 mm |
| Wavelength: | 319.1 nm |
| Flame Conditions: | $N_2O - C_2H_2$ (rich) |
| Burner Height Setting: | 12.2 |
| Burner Horizontal Setting: | 2.5 |
| Fuel Flow Meter: | 4.7 |
| $N_2O$ Flow Meter: | 5.2 |
| Fuel Pressure: | 8 psi |
| $N_2O$ Pressure: | 30 psi |
| Sensitivity: | 1.6 µ gm/ml |
| Detection Limit: | 0.05 µ gm/ml |

The parts per million of vanadium detected in Sample A and Sample B for this set of measurements (41-50) are graphically presented in

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Figure 2. Values obtained earlier are included for ease of referral. The mean and standard deviation are listed in Table 1 for each set of vanadium measurements made on these sediment samples.

2. Cadmium

| | |
|---|---|
| H.C. Lamp Current: | 10.5 ma |
| Slit Width (4): | 1.0 mm |
| Wavelength: | 229.6 nm |
| Flame Conditions: | Air – $C_2H_2$ (lean) |
| Burner Height Setting: | 13.3 |
| Burner Horizontal Setting: | 2.7 |
| Fuel Flow Meter: | 9.5 |
| Air Flow Meter: | 9.0 |
| Fuel Pressure: | 8 psi |
| Air Pressure: | 30 psi |
| Sensitivity | 0.050 μ gm/ml |
| Detection Limit: | 0.001 μ gm/ml |

The ten determinations (measurements 34-43) of cadmium content in Sample A and Sample B were higher than the 33 replicate analyses performed previously as shown in Table 2 and Figure 3. The increase in cadmium concentration is not significant as will be shown in a later set of measurements of these same acid extracts of Sample A and Sample B.

Figure 2. Replicate Analysis of SRM A and B for Vanadium by Flame AAS. Acid extracts of the sediments were analyzed; results presented on a dry weight basis and calculated by direct comparison to aqueous standards.

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| Sample | Number of Measurements | Mean Concentration (ppm) | Standard Deviation (ppm) |
|--------|------------------------|--------------------------|--------------------------|
| A | 1 thru 20 | 27.1 | 9.5 |
| A | 21 thru 28 | 24.8 | 2.0 |
| A | 29 thru 40 | 33.0 | 6.0 |
| A | 41 thru 50 | 28.8 | 4.1 |
| | | | |
| B | 1 thru 20 | 8.1 | 0.3 |
| B | 21 thru 28 | 8.4 | 2.4 |
| B | 29 thru 40 | 8.3 | 0.04 |
| B | 41 thru 50 | 9.0 | 2.4 |

Table 1.  Mean and Standard Deviation Values for Vanadium Content in SRM Sediments A and B.  The data is shown in graphic form in figure 2.

| Sample | Number of Measurements | Mean Concentration (ppm) | Standard Deviation (ppm) |
|--------|------------------------|--------------------------|--------------------------|
| A | 1 thru 5 | 0.25 | 0.04 |
| A | 6 thru 16 | * | * |
| A | 17 thru 21 | 0.25 | 0.04 |
| A | 22 thru 33 | 0.23 | 0.05 |
| A | 34 thru 43 | 0.34 | 0.04 |
| | | | |
| B | 1 thru 5 | 0.98 | 0.42 |
| B | 6 thru 16 | 1.20 | 0.25 |
| B | 17 thru 21 | 1.03 | 0.18 |
| B | 22 thru 33 | 1.17 | 0.25 |
| B | 34 thru 43 | 1.39 | 0.10 |

* Below minimum detection limit

Table 2. Mean and Standard Deviation Values for Cadmium Content in SRM Sediments A and B. The data is shown in graphic form in figure 3.
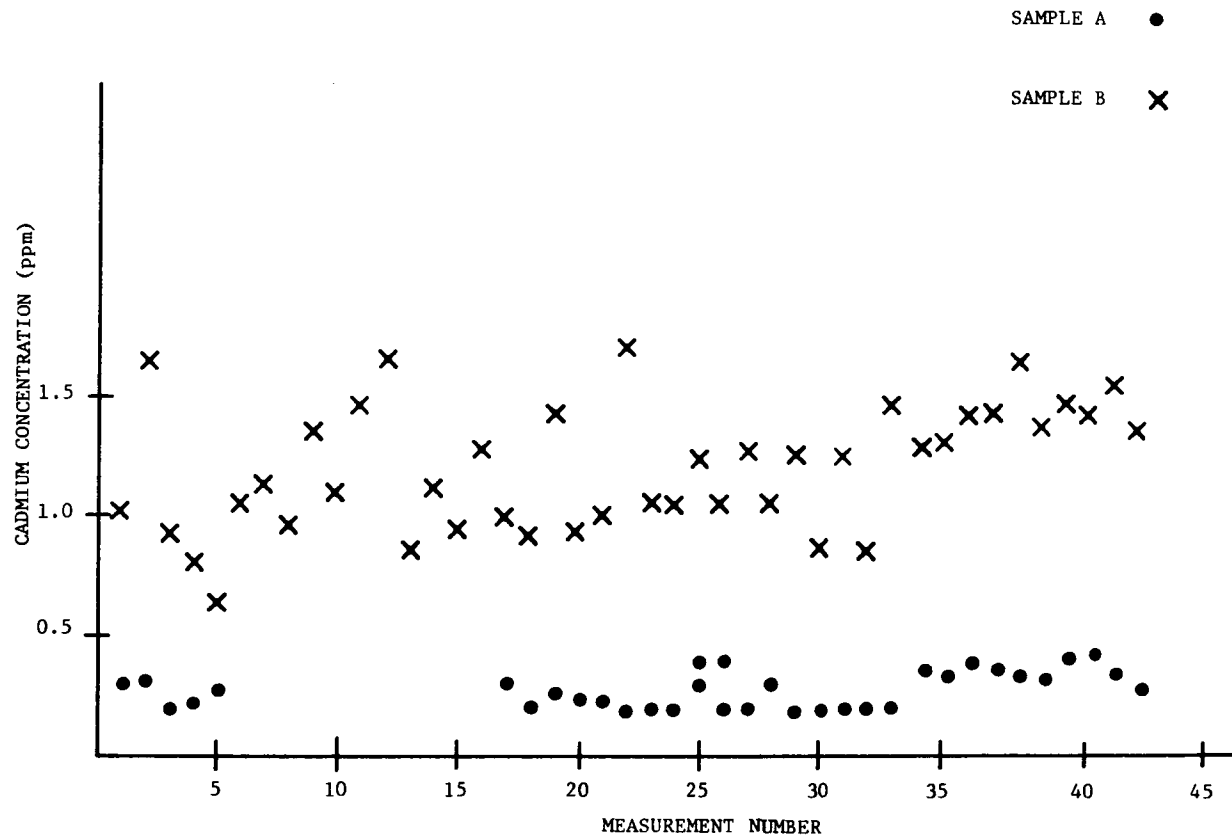
Figure 3. Replicate Analysis of SRM A and B for Cadmium by Flame AAS. Acid extracts of the sediment were analyzed; results presented on a dry weight basis and calculated by direct comparison to aqueous standards.

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3. Lead

| | |
|---|---|
| H.C. Lamp Current: | 10 ma |
| Slit Width (4): | 1.0 mm |
| Wavelength: | 284.1 nm |
| Flame Conditions: | Air – $C_2H_2$ (lean) |
| Burner Height Setting: | 12.5 |
| Burner Horizontal Setting: | 2.5 |
| Fuel Flow Meter: | 8.7 |
| Air Flow Meter: | 10.0 |
| Fuel Pressure: | 8 psi |
| Air Pressure: | 30 psi |
| Sensitivity: | 0.9 μgm/ml |
| Detection Limit: | 0.05 μgm/ml |

The mean and standard deviation values calculated for lead content in measurements 35-44 of Sample A and Sample B are given in Table 3. The mean for Sample A is higher than earlier determinations while the mean for Sample B is lower. The observed differences, however, are not statistically significant. Measurements 35-44 are shown graphically in Figure 4.

4. Nickel

| | |
|---|---|
| H.C. Lamp Current: | 22 ma |
| Slit Width (4): | 1.0 mm |
| Wavelength: | 232.8 nm |
| Flame Conditions: | $N_2O$ – $C_2H_2$ (lean) |

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| Sample | Number of Measurements | Mean Concentration (ppm) | Standard Deviation (ppm) |
|--------|------------------------|--------------------------|--------------------------|
| A | 1 thru 5 | 20.4 | 2.1 |
| A | 6 thru 16 | 20.8 | 1.9 |
| A | 17 thru 21 | 20.4 | 0.2 |
| A | 22 thru 34 | 21.5 | 1.6 |
| A | 35 thru 44 | 24.0 | 3.7 |
| B | 1 thru 5 | 8.0 | 2.5 |
| B | 6 thru 16 | 9.0 | 1.6 |
| B | 17 thru 21 | 10.0 | 1.0 |
| B | 22 thru 34 | 9.2 | 1.0 |
| B | 35 thru 44 | 7.9 | 1.5 |

Table 3. Mean and Standard Deviation Values for Lead Content in SRM Sediments A and B. The data is shown in graphic form in figure 4.
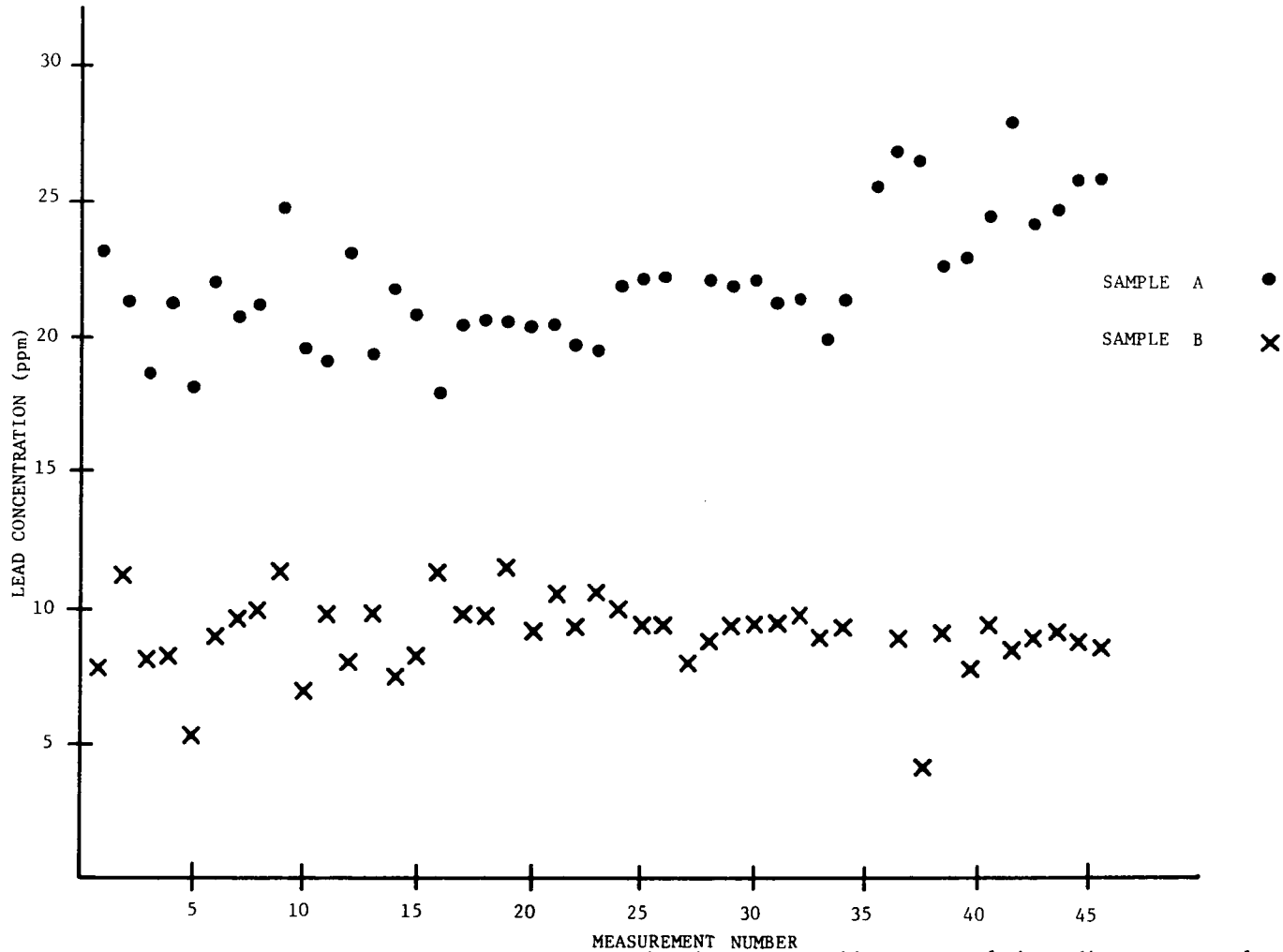
Figure 4. Replicate Analysis of SRM A and B for Lead by Flame AAS. Acid extracts of the sediment were analyzed; results obtained on a dry weight basis and calculated by direct comparison.

| | |
|---|---|
| Burner Height Setting: | 12.2 |
| Burner Horizontal Setting: | 2.7 |
| Fuel Flow Meter: | 4.7 |
| $N_2O$ Flow Meter: | 5.2 |
| Fuel Pressure: | 8 psi |
| $N_2O$ Pressure: | 29.5 psi |
| Sensitivity: | 1.0 μgm/ml |
| Detection Limit: | 0.02 μgm/ml |

The nitrous oxide-acetylene flame is used for all nickel measurements despite the significant three-fold loss in sensitivity and contrary to the manufacturer's suggestions. The comparison study (BLM Progress Report I) of the percent recovery of known nickel additions using the air-acetylene versus nitrous oxide-acetylene flame demonstrated the enhanced accuracy of the latter flame system. As a result the detection limit was exceeded for Sample B (Table 4) for measurements 34-43. The analysis of Sample A, measurements 34-43, agreed well with measurements 22-33 performed earlier with the same flame system. These latter 21 determinations performed with the nitrous oxide-acetylene flame, are significantly lower than the first 21 measurements made with the air-acetylene flame system (Figure 5).

5. Copper

| | |
|---|---|
| H.C. Lamp Current: | 15 ma |
| Slit Width (4): | 1.0 mm |

| Sample | Number of Measurements | Mean Concentration (ppm) | Standard Deviation (ppm) |
|--------|------------------------|--------------------------|--------------------------|
| A | 1 thru 5 | 6.9 | 1.1 |
| A | 6 thru 16 | 5.9 | 0.8 |
| A | 17 thru 21 | 7.9 | 0.7 |
| A | 22 thru 33 | 4.6 | 1.2 |
| A | 34 thru 43 | 4.5 | 0.9 |
| B | 1 thru 5 | 1.3 | 0.6 |
| B | 6 thru 16 | 0.6 | 0.02 |
| B | 17 thru 21 | 2.8 | 1.3 |
| B | 22 thru 26 | 1.0 | 0 |
| B | 27 thru 33 | * | * |
| B | 34 thru 43 | * | * |

* Below minimum detection limit

Table 4. Mean and Standard Deviation Values for Nickel Content in SRM Sediments A and B. The data is shown in graphic form in figure 5.

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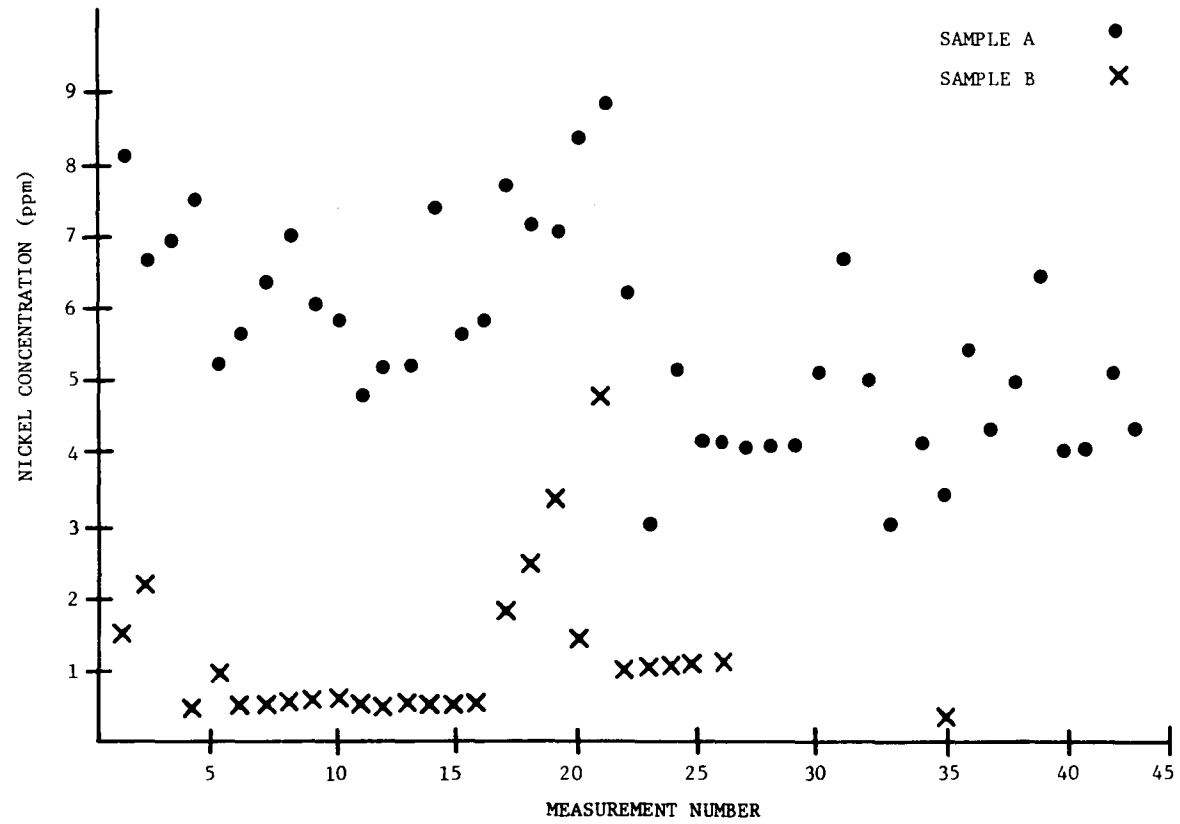
Figure 5.  Replicate Analysis of SRM A and B for Nickel by Flame AAS.  Acid extracts of the sediments were analyzed ; results obtained on a dry weight basis and calculated by direct comparison to aqueous standards.

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| | |
|---|---|
| Wavelength | 325.6 nm |
| Flame Conditions: | Air - $C_2H_2$ (lean) |
| Burner Height Setting: | 13.5 |
| Burner Horizontal Setting: | 3.7 |
| Fuel Flow: | 9.5 |
| Air Flow: | 9.3 |
| Fuel Pressure: | 8 psi |
| Air Pressure: | 30 psi |
| Sensitivity: | 0.1 µgm/ml |
| Detection Limit: | 0.003 µgm/ml |

The ten replicate analyses (34-43) of copper content in Sample A and Sample B are shown graphically in Figure 6. The mean and standard deviation is given in Table 5. The increase in standard deviation and decrease in mean copper concentration for Sample B compared to the previous two sets of determinations is apparent and is discussed in the next section (chromium).

6. Chromium

| | |
|---|---|
| H.C. Lamp Current: | 18.5 ma |
| Slit Width (3): | 0.3 mm |
| Wavelength: | 358.5 nm |
| Flame Conditions: | $N_2O$ - $C_2H_2$ (rich) |
| Burner Height Setting: | 13.2 |
| Burner Horizontal Setting | 2.5 |
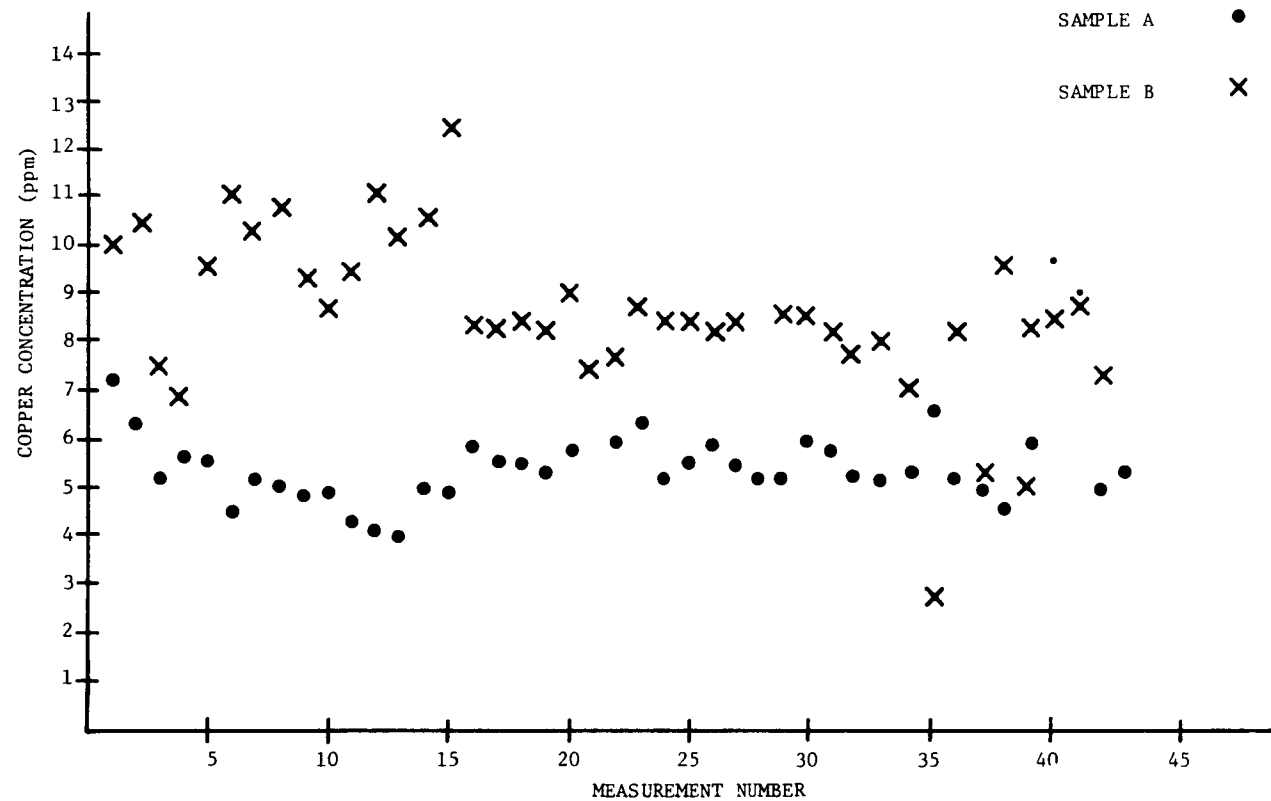
Figure 6. Replicate Analysis of SRM A and B for Copper by Flame AAS. Acid extracts of the sediments were
analyzed; results obtained on a dry weight basis and calculated by direct comparison to aqueous standards.

| Sample | Number of Measurements | Mean Concentration (ppm) | Standard Deviation (ppm) |
|---|---|---|---|
| A | 1 thru 5 | 6.0 | 0.8 |
| A | 6 thru 16 | 4.7 | 0.4 |
| A | 17 thru 21 | 5.4 | 0.3 |
| A | 22 thru 33 | 5.6 | 0.4 |
| A | 34 thru 43 | 6.3 | 1.8 |
| B | 1 thru 5 | 8.7 | 1.6 |
| B | 6 thru 16 | 10.8 | 1.7 |
| B | 17 thru 21 | 8.5 | 0.2 |
| B | 22 thru 33 | 8.3 | 0.3 |
| B | 34 thru 43 | 7.2 | 2.0 |

Table 5. Mean and Standard Deviation Values for Copper
Content in SRM Sediments A and B. The data
is shown in graphic form in figure 6.

| Fuel Flow Meter: | 4.7 |
|---|---|
| $N_2O$ Flow Meter | 5.0 |
| Sensitivity: | 0.5 $\mu$gm/ml |
| Detection Limit: | 0.1 $\mu$gm/ml |

The chromium concentration for measurements 30-39 is graphically presented in Figure 7; the mean and standard deviation is given in Table 6. The concentration calculated for Sample B, Measurement 31 is dramatically lower than the other nine replicate Sample B determinations. Inspection of the values obtained with this extract for vanadium, cadmium, lead, nickel, and copper demonstrates that this sample is clearly out-of-control statistically (Table 7, Figures 2 through 7). It can be postulated that the cause for the erroneous values obtained for this extract was improper dilution of the digest to 100 ml instead of 50 ml. The metal content in all cases, except cadmium, is approximately 50% of the mean concentration value. In addition, more convincing evidence can be obtained by noting that nickel content was detected only in this extract due to decreased interferent levels. Even though the deviation observed with this extract can be logically explained, the values for each metal must be discarded from a statistical standpoint and the analysis repeated.
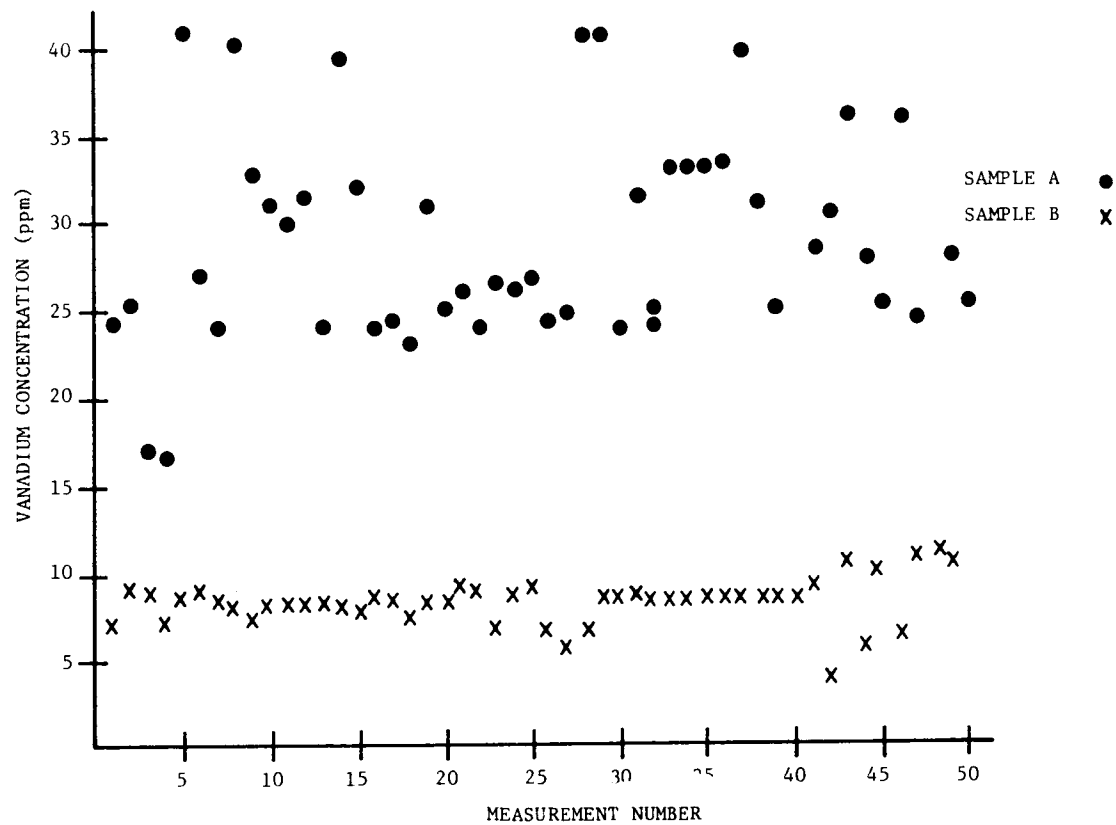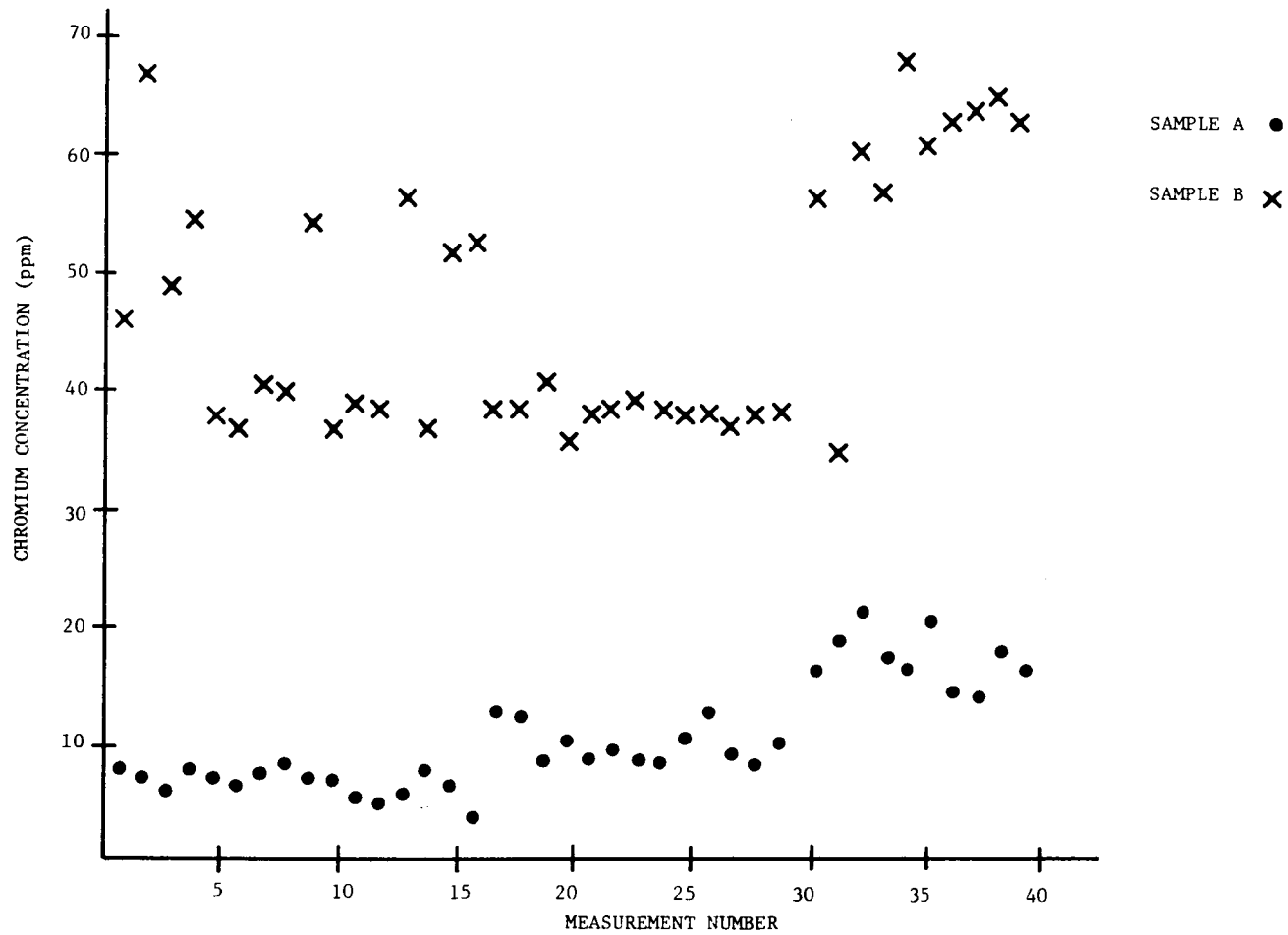
Figure 7. Replicate Analysis of SRM A and B for Chromium by Flame AAS. Acid extracts of the sediments were analyzed; results obtained on a dry weight basis and calculated by direct comparison to aqueous standards.

| Sample | Number of Measurements | Mean Concentration (ppm) | Standard Deviation (ppm) |
|--------|------------------------|--------------------------|--------------------------|
| A | 1 thru 5 | 7.7 | 0.7 |
| A | 6 thru 16 | 7.0 | 1.4 |
| A | 17 thru 29 | 10.4 | 1.7 |
| A | 30 thru 39 | 17.0 | 2.4 |
| B | 1 thru 5 | 51.3 | 10.9 |
| B | 6 thru 16 | 44.5 | 8.0 |
| B | 17 thru 29 | 38.6 | 1.2 |
| B | 30 thru 39 | 58.1 | 9.7 |

Table 6.  Mean and Standard Deviation Values for Chromium Content in SRM Sediments A and B.  The data is shown in graphic form in figure 7.

| Metal | Corresponding Measurement No. (Figure) | Metal Content (ppm) | Mean | Standard Deviation | *Mean | Standard Deviation* |
|---|---|---|---|---|---|---|
| V | 42 (2) | 4.1 | 9.0 | 2.4 | 9.6 | 2.0 |
| Cd | 35 (3) | 1.3 | 1.4 | 0.1 | 1.4 | 0.1 |
| Pb | 36 (4) | 3.7 | 7.9 | 1.5 | 8.4 | 0.6 |
| Ni | 35 (5) | 0.4 | † | † | † | † |
| Cu | 35 (6) | 2.9 | 7.2 | 2.0 | 7.8 | 1.1 |
| Cr | 31 (7) | 34.1 | 58.1 | 9.7 | 61.1 | 3.9 |

* Statistical analysis excluding out-of-control sample.

† Detection limit exceeded.

Table 7. Calculation of Trace Metal Values Obtained for One Extract (Sample B) Judged Out-of-Control. Results in ppm on a dry weight basis and graphically illustrated in figures 2 - 7.

## 2. Barium by the Method of Standard Additions

The confirmation of barium Standard Additions experiments for Sample A and Sample B presented in Progress Report I is included here. The amount of barium measured in Sample A was observed to vary from 40 ppm to 100 ppm while that for Sample B increased from 14 ppm to 27 ppm. The higher barium measurements were attributed to elimination of existing interferences due to iron and aluminum. Larger sample volumes were used for this experiment since the 2 ml and 3 ml aliquots used in the earlier study could have been subject to some error by dilution. The experimental conditions are as follows for Sample A:

| | Final Conc. of | | | Absorbance Measured | |
| ml Sample A | Barium Added ml (ppm) | Dilution Volume (ml) | Sample A | Aqueous Standard | Matrix-Matched Standard |
|---|---|---|---|---|---|
| 15 | 0 | 25 | .009 | .000 | .000 |
| 15 | 2 | 25 | .012 | .005 | .003 |
| 15 | 4 | 25 | .018 | .010 | .006 |
| 15 | 6 | 25 | .021 | .015 | .010 |

For Sample B:

| | Final Conc. of | | | | |
| ml Sample B | Barium Added ml (ppm) | Dilution Volume (ml) | Sample B | Aqueous Standard | Matrix-Matched Standard |
|---|---|---|---|---|---|
| 15 | 0 | 25 | .001 | .000 | .000 |
| 15 | 2 | 25 | .004 | .005 | .003 |
| 15 | 4 | 25 | .008 | .010 | .006 |
| 15 | 6 | 25 | .012 | .015 | .010 |

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The plot of absorbance versus concentration of barium additions is presented in Figure 8 for Sample A and Figure 9 for Sample B. The aqueous standard curve is included in the graph for Sample A to illustrate the non-parallel relationship observed for two solutions of differing matrices. The barium concentration measured for the reference Sediments A and B is given in Table 8. The values obtained earlier after matrix correction are given for comparison purposes. Several attempts to measure barium concentration using the method of Standard Additions were unsuccessful chiefly due to use of small aliquots of sample digestion. A broad range of values were obtained until the use of larger aliquots and minimum dilution of the sample aliquots was adopted.
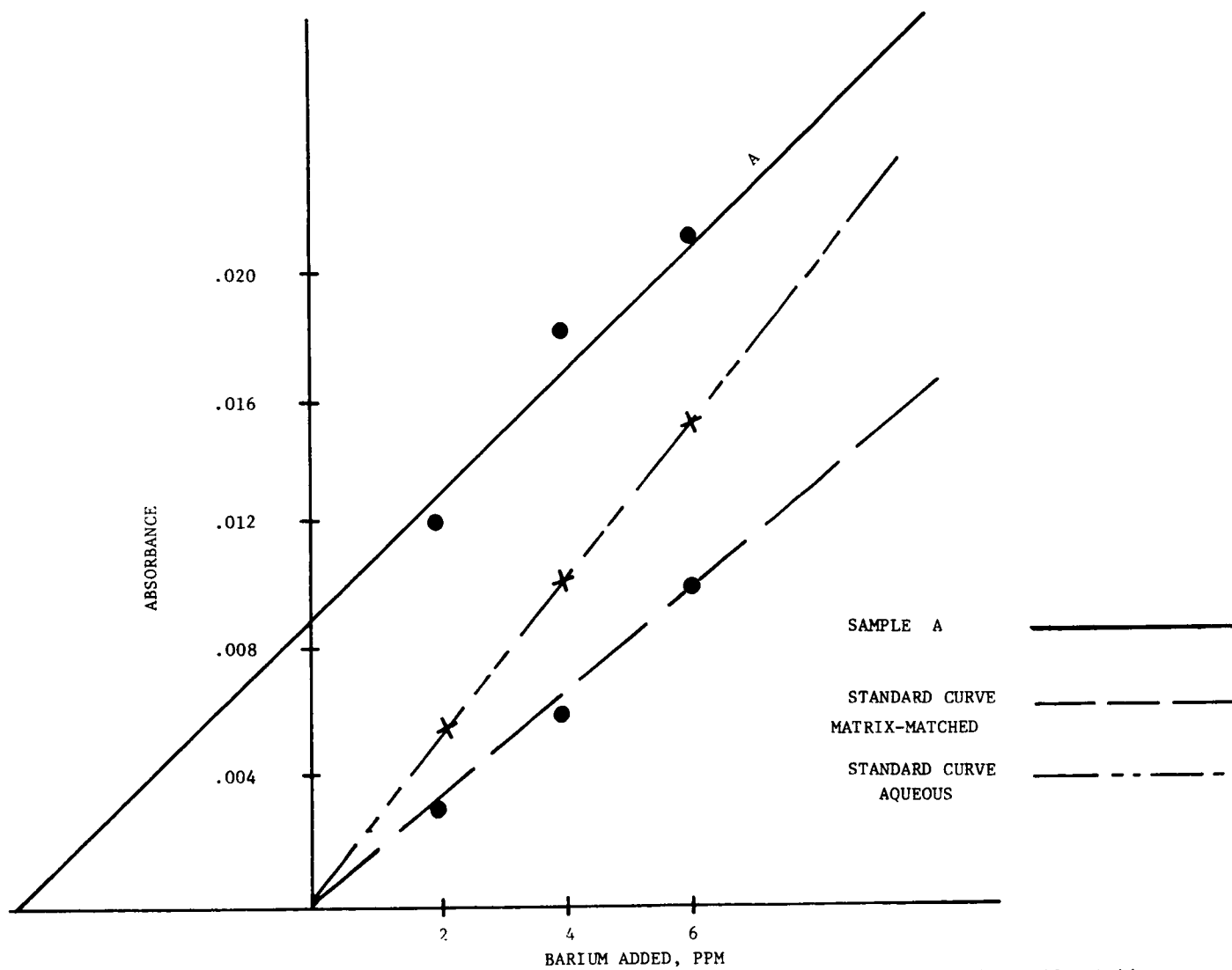
Figure 8. Standard Addition Curve for Analysis of SRM Sediment A for Barium by Flameless AAS.   Acid extracts
of the sediments were analyzed and results obtained on a dry weight basis ;  data obtained by direct comparison
to aqueous and matrix-matched standards.
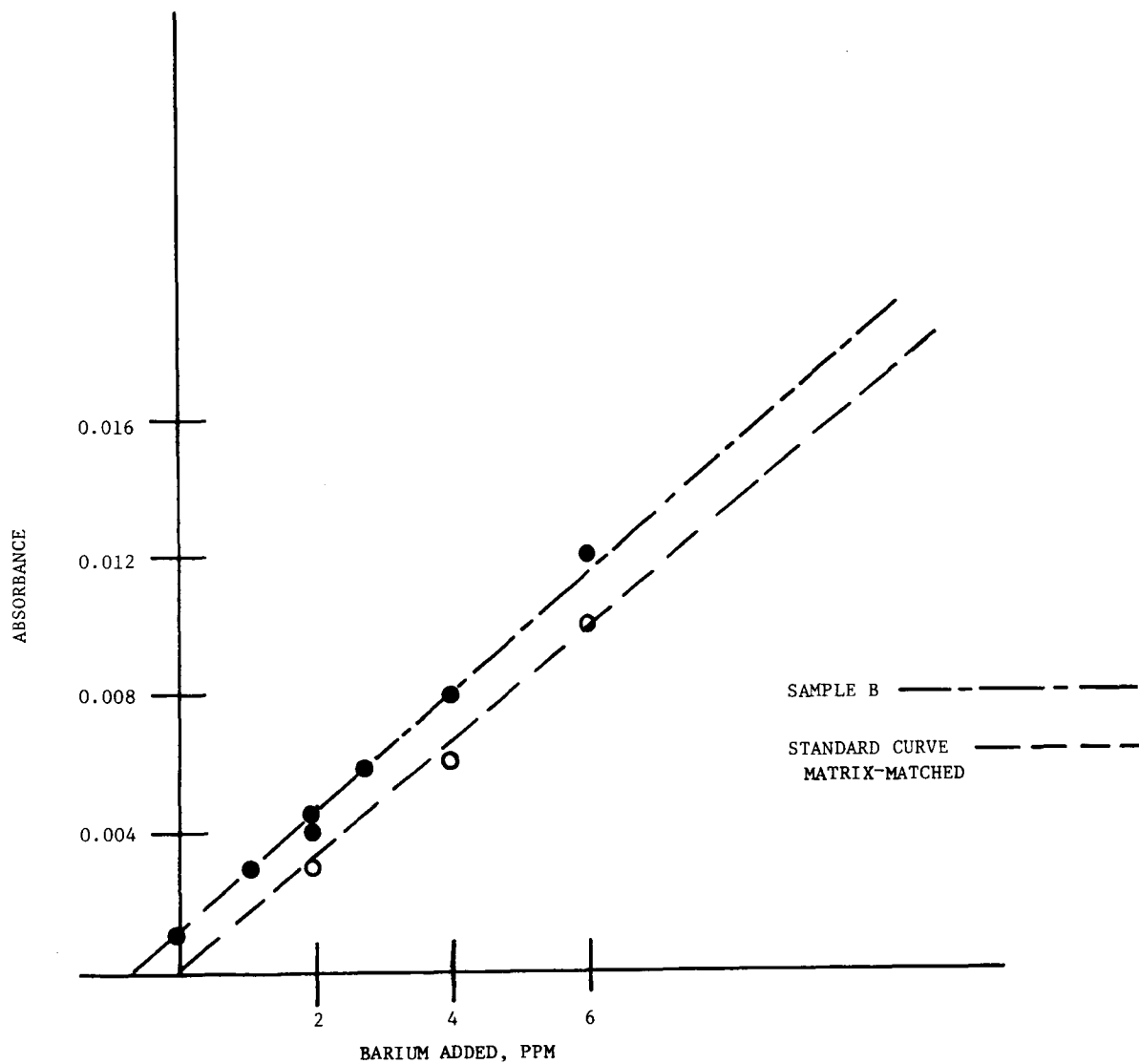
Figure 9. Standard Addition Curve for Analysis of SRM Sediment B for Barium by Flame AAS. Acid extracts of the sediments were analyzed and results obtained on a dry weight basis ; data obtained by direct comparison to aqueous and matrix-matched standards.

| Method | Sample A | Sample B |
|---|---|---|
| Graphical (X-intercept) | 96.3 | 20.5 |
| Mathematical<br>(Average of 2 ppm, 4 ppm,<br>6 ppm Spikes) | 102.0 | 21.0 |
| Comparison with Standards:<br>  Aqueous<br>  Matrix-Matched | 74.6<br>93.8 | 16.5<br>20.8 |
| *Mean | 97.4 | 20.8 |
| †Mean (obtained earlier –<br>  Progress Report I) | 97.5 | 26.6 |

* Value omitted for comparison with aqueous standards.

† Excluding values for this analysis; presented for comparison purposes only

Table 8.  Calculation of Barium Concentration in SRM Sediments
A and B.  Results in ppm on a dry weight basis.

## 3. Vanadium by the Method of Standard Additions

Vanadium Standard Additions plots exhibited evidence of
matrix interferences to the same degree as barium. However,
while barium absorbance was suppressed due to the interferents,
vanadium absorbance was enhanced. The Standard Additions experiments
reported earlier were repeated since vanadium measurements by
Atomic Absorption Spectrophotometry demonstrate poor sensitivity.
The experimental conditions were as follows for Sample A and
Sample B:

| ml Sample A & B | Final Conc. of Vanadium Added (ppm) | Dilution Volume (ml) | Sample A | Sample B | Matrix-Matched Standards |
|---|---|---|---|---|---|
| 15 | 0 | 25 | 0.63 | 0.66 | 0 |
| 15 | 2 | 25 | 1.85 | 1.30 | 1.11 |
| 15 | 4 | 25 | 3.10 | 2.50 | 2.10 |
| 15 | 6 | 25 | 3.80 | 3.29 | 3.13 |

The peak height measured on a strip chart recorder is presented
rather than absorbance readings since the unspiked samples exhibited
absorbance of 0.001 (Sample A) and 0.003 (Sample B). The similar
peak heights measured are not different by a factor of 3 as indicated
by the absorbance readings. The graphical representation of the
vanadium Standard Additions experiment are shown in Figure 10 and
Figure 11 for Sample A and Sample B, respectively. The matrix-matched
standard curve is not parallel to the sample curve suggesting in-
adequate matrix-matching. The points deviated from the curve more
than expected for this procedure. This behavior can be ascribed to
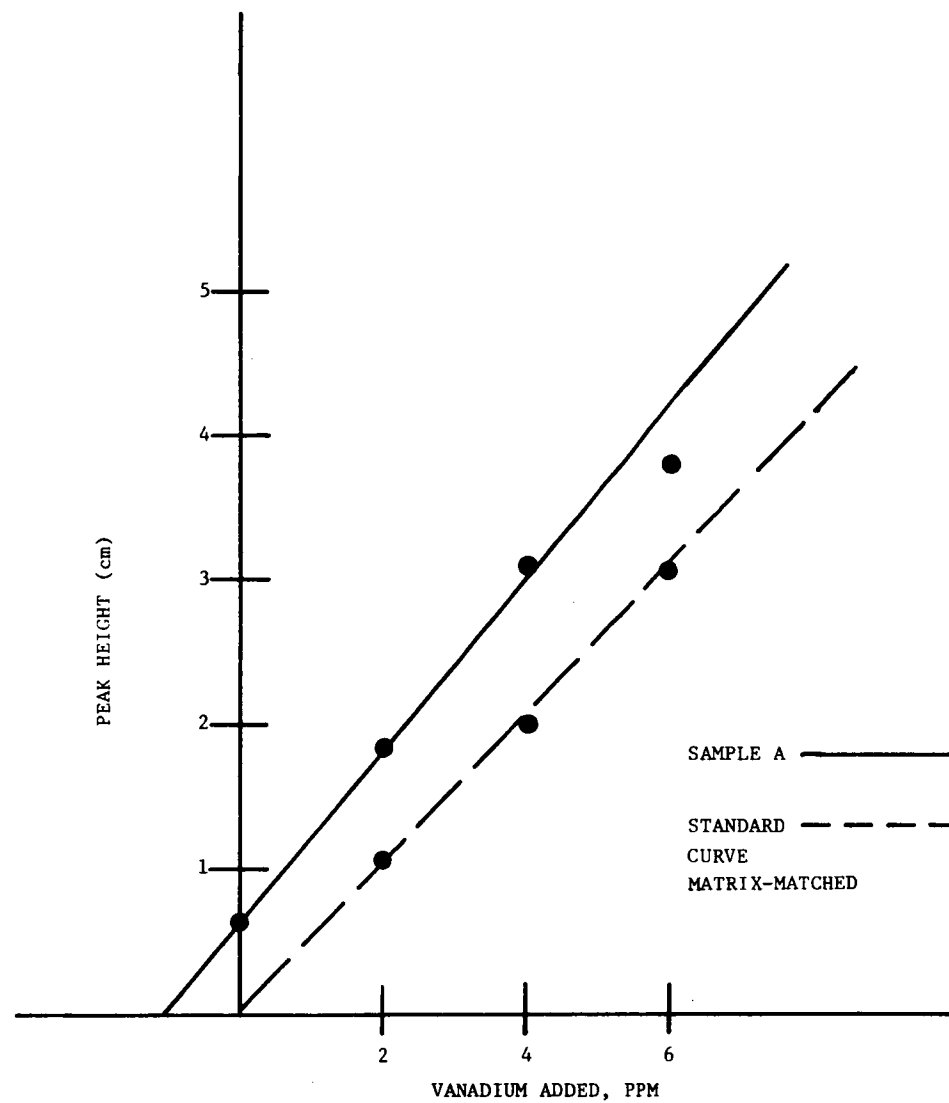
Figure 10.  Standard Addition Curve for Analysis of SRM Sediment A for Vanadium by Flame AAS.  Acid extracts of the sediments were analyzed and results obtained on a dry weight basis ; data obtained by direct comparison to aqueous and matrix-matched standards.

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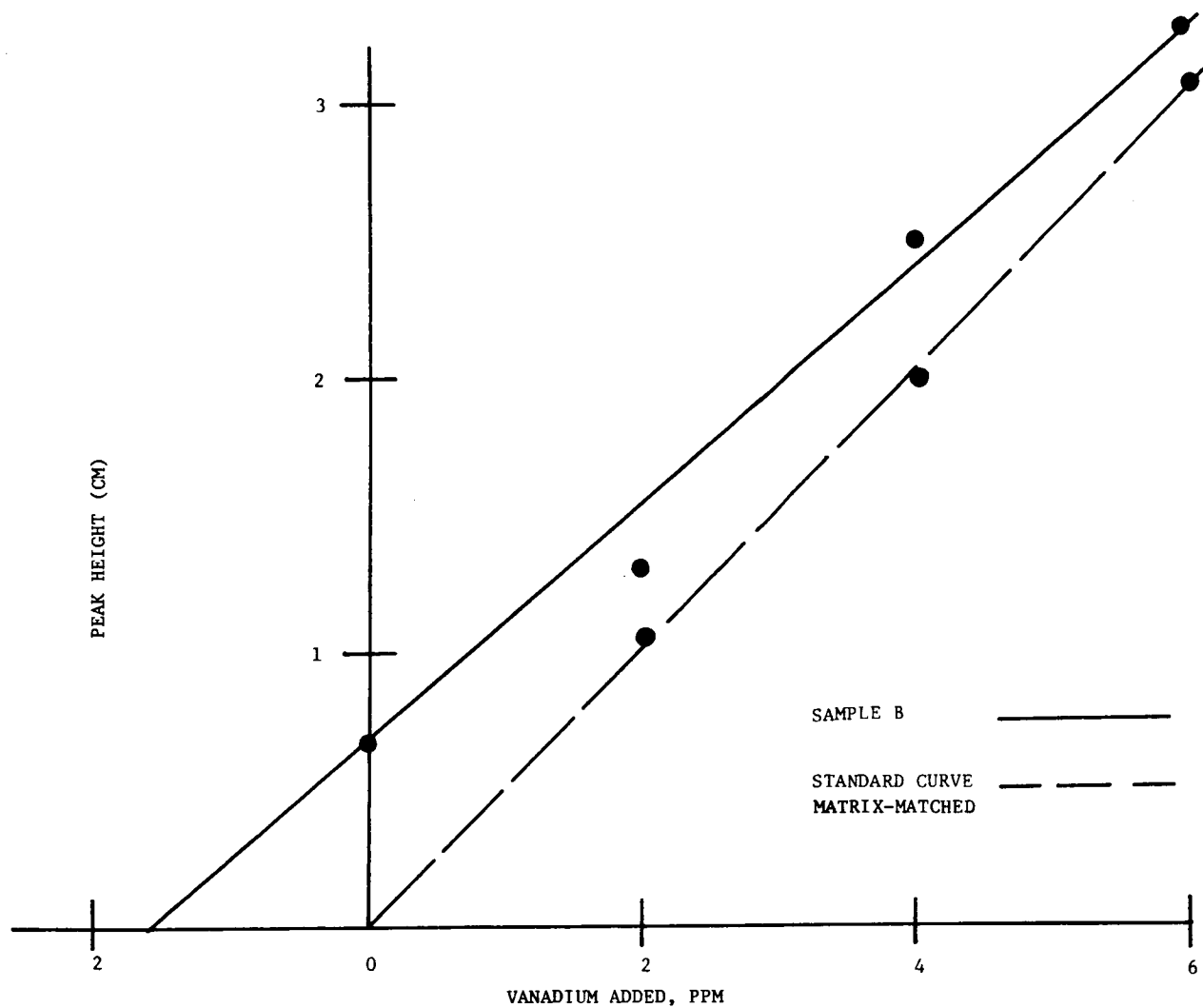
Figure 11. Standard Addition Curve for Analysis of SRM Sediment B for Vanadium by Flame AAS. Acid extracts of the sediments were analyzed and results obtained on a dry weight basis ; data obtained by direct comparison to aqueous and matrix-matched standards.

the combination of poor sensitivity, low concentration of vanadium in solution, and necessary multiple dilutions. The concentration of vanadium measured for Samples A and B is presented in Table 9 for several methods of calibration. The concentration of vanadium in Sample A agrees with the value reported earlier while that measured in Sample B is higher by a factor of 2. Several Standard Addition experiments were performed for determination of vanadium content in these reference samples. The resultant concentrations ranged from 3 to 25 ppm for Sample A and from 11 to 33 ppm for Sample B.

| Method | Sample A | Sample B |
|--------|----------|----------|
| Graphical (X-intercept) | 20.7 | 27.2 |
| Mathematical (Average) | 22.4 | 28.4 |
| Comparison with Standards (Average) | | |
|    Aqueous | 28.4 | 24.5 |
|    Matrix-Matched | 24.4 | 21.1 |
| Mean | 24.7 | 25.3 |
| *Mean (Obtained earlier - Progress Report I) | 27.8 | 16.3 |

*Excluding values for this analysis; presented for comparison purposes only.

Table 9. Calculation of Vanadium Concentrations in SRM Sediments A and B. Results in ppm on a dry weight basis.

## 4. Aqueous Standards vs. Matrix-Matched Standards

The ten replicate acid digests of Sample A and Sample B were analyzed in Experiment I by calibrating the Atomic Absorption Spectrophotometer with aqueous standards. The same 20 acid digests were analyzed again for each element using standards containing the amounts of iron and aluminum in the sample matrix to calibrate the instrument. Since Sample A and Sample B contain significantly different quantities of iron and aluminum, a separate set of standards was made for sediment A and sediment B acid digests. The same set of aqueous standards was used for both Sample A and Sample B replicate analyses. The instrumental parameters employed were identical to those described for each element in Experiment I.

An increase or decrease in mean trace metal content was observed when matrix-matched standards were employed except for lead. The means calculated for the two types of standards are presented in Table 10 for Sample A and Table 11 for Sample B. Iron measurements were not made by this method since iron is presented in greater than trace amounts. Barium was not determined because it would have been necessary to add potassium to the samples to control ionization effects thus altering the matrix.

## B. MATRIX ANALYSIS - MAFLA SEDIMENT SAMPLES

## 1. Preliminary Remarks

The matrix of environmental samples such as sediment is known to vary considerably from area to area. The relative quantities of both

| Trace Metal | Mean Concentration for Aqueous Standard Calibration | Mean Concentration for Matrix-Matched Standard Calibration | % Net Change [*] |
|---|---|---|---|
| V | 28.8 | 24.1 | − 16.3 |
| Cd | 0.34 | 0.25 | − 26.5 |
| Pb | 24.0 | 24.0 | 0 |
| Ni | 4.5 | 5.9 | + 31.1 |
| Cu | 6.3 | 2.2 | − 65.1 |
| Cr | 17.0 | 15.5 | − 8.8 |

*Relative to values obtained via aqueous standards.

Table 10. Mean Trace Metal Concentrations Calculated for SRM Sediment A. Data reported in ppm on a dry weight basis and calculated against aqueous versus matrix-matched standards.

| Trace Metal | Mean Concentration for Aqueous Standard Calibration | Mean Concentration for Matrix-Matched Standard Calibration | % Net Change* |
|---|---|---|---|
| V | 9.6 | 8.3 | - 13.5 |
| Cd | 1.4 | 1.2 | - 14.3 |
| Pb | 8.4 | 8.4 | 0 |
| Ni | † | † | * |
| Cu | 7.4 | 6.4 | - 13.5 |
| Cr | 61.1 | 58.0 | - 5.1 |

*Relative to values obtained via aqueous standards.

† Detection limit exceeded.

Table 11.  Mean Trace Metal Concentrations Calculated for SRM
Sediment B.  Data shown is excluding sample judged
out-of-control and is reported on a dry weight basis
in ppm.

major (>1%) constituents and trace (<0.1%) constituents in environmental
samples is dependent upon the geological makeup of the particular
sampling site (30). It is reasonable to assume that geographical
location is of prime importance. Marine sediments would not,
therefore, be expected to contain the same precentages of potential
Atomic Absorption Spectrophotometric interferents as bottom sediments
collected from fresh water systems. Similarly, variation in sediment
content is predicted from one marine location to another.

The observed effect upon trace metal analyses for major con-
stituents such as iron and aluminum is significant. Erroneous
analyses are certain to occur that will ultimately lead to incorrect
data interpretation. Prior to collection of quality control data for
the MAFLA Environmental Baseline Survey the matrix of the 35 sediment
samples was defined. The insufficient quantity of sediment received
(10 grams) precluded extensive matrix analysis of each sediment for
both major and trace metal determinations.

Two groupings of small aliquots of each sediment were chosen for
matrix analysis. Group I A through VII A was formed by mixing one
gram of each of the 35 sediment samples in groups of five arranged in
numerical order as shown in Figure 12. The second grouping, Group I B
through VII B was made by combining five 0.5 gram aliquots of each
of five randomly chosen sediments as shown in Figure 12. Group A and
Group B were prepared and analyzed separately in order to minimize
the possibility of sample loss.

| Group A (∿ 5 grams) | BLM MAFLA Sediment I.D. | Group B (∿ 2.5 grams) |
|---|---|---|
| | 1 | |
| | 2 | |
| I A | ৭ | I B (3, 6, 25, 30, 44) |
| (4.3285 g) | 5 | (2.4635 g) |
| | 6 | |
| | 7 | |
| II A | 9 | IJ B (19, 24, 29, 36, 48) |
| (4.7815 g) | 11 | (2.2730 g) |
| | 13 | |
| | 16 | |
| | 19 | |
| III A | 22 | III B (19, 24, 29, 36, 48) |
| (4.6341 g) | 24 | (2.3866 g) |
| | 25 | |
| | 26 | |
| | 27 | |
| IV A | 28 | IV B (13, 26, 34, 39, 57) |
| (5.0910 g) | 29 | (2.4225 g) |
| | 30 | |
| | 32 | |
| | 33 | |
| V A | 34 | V B (16, 28, 33, 38, 49) |
| (5.2969 g) | 36 | (2.4376 g) |
| | 38 | |
| | 39 | |
| | 41 | |
| VI A | 42 | V B (?, 7, 11, 60, 63) |
| (5.3812 g) | 44 | (2.4125 g) |
| | 48 | |
| | 49 | |
| | 54 | |
| VII A | 56 | VII B (1, 4, 22, 32, 41) |
| (4.9071 g) | 57 | (2.4108) |
| | 60 | |
| | 63 | |

Figure 12.  Groupings of MAFLA Sediments for Matrix Analysis.

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The first difficulty attributable to differences in matrix was encountered early in the procedure. The seven group A sediments were placed in 250 ml beakers for digestion with nitric acid, hydrochloric acid, and distilled water. Upon addition of the acids to the sediments, the samples vigorously foamed indicating an unusally high concentration of carbonate. The observed foaming resulted in the loss of three of the composite samples (VA, VIA, VIIA) when the quantity of foam produced exceeded the volume of the 250 ml beakers. If the prepared composite samples had not been analyzed before the actual sediment samples, an entire analysis "set" (8-10) of the sediments could have been lost although the federally recommended procedure was followed. The method of reagent addition that minimizes foaming action is simply the addition of water first followed by slow, dropwise addition of $HNO_3$ and HCl. Specific modification of the federally recommended sediment digestion procedure is indicated in order to avoid occurrences of this nature.

2. Major Constituents

Metals present in environmental samples in large concentrations may adversely affect trace metal determinations by Atomic Absorption Spectrophotometry. The degree of interference effect is dependent upon the concentration and type of interferent. It was desirable for purposes of expediency that the MAFLA sediment matrix be comparable to the matrix in the sediments used for reference standards (Sample A and Sample B).

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The composite MAFLA sediment samples were analyzed for all metals

for which reported average earth crust values exceeded 20,000 ppm

(2%).  The major analytes include:  aluminum, calcium, iron,

magnesium, sodium, silicon, and potassium.  The concentration

measurements are presented for the first four composite samples in

Group A in Table 12.  The average earth crust values and the amounts

previously determined for Sample A and Sample B are included for

comparison.  The MAFLA sediment composites contain comparable

quantities of iron and aluminum as the reference sediments Sample A

and Sample B.  The most marked difference in matrix makeup is apparent

for calcium content; the amount observed is extremely high for the

MAFLA composites compared to either of the two reference sediments.

The analysis of the second set of MAFLA composites was more complete

since none of the samples were lost as a consequence of foaming

during initial stages of the digestion process.  The determination of

the matrix of the Group B composites was performed to confirm the

Group A analysis.  In addition, since different sediments were combined,

a difference in concentration of a particular analyte due to one or

two individual MAFLA sediments could be observed.  Identification of

such a sample is possible by comparison of the groupings in Figure 12.

The concentrations of the seven major constituents of interest

for Group B are given in Table 13.  Averages were calculated in order

to compare the two sample selection procedures for the composites.

It is difficult to identify specific trends by comparing the

matrix analysis of the two composite sets for major constituents.  A

few comparisons do appear to be valid:

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| Metal | Average Earth Crust | Reference Sample A | Reference Sample B | MAFLA Composite Group A Sediment Samples* $I_A$ | $II_A$ | $III_A$ | $IV_A$ |
|---|---|---|---|---|---|---|---|
| Al | 82,000 | 15,600 | 3,200 | 4,390 | 9,935 | 5,400 | 3,650 |
| Ca | 41,500 | 56 | 12 | 135,440 | 127,440 | 162,385 | 220,730 |
| Fe | 56,300 | 8,500 | 1,500 | 15,744 | 2,330 | 5,240 | 5,670 |
| Mg | 23,300 | 1,800 | 540 | 78,090 | 7,500 | 14,080 | 15,910 |
| Na | 23,600 | 250 | 60 | 5,580 | 2,010 | 8,080 | 6,875 |
| Si | 281,500 | 160 | 70 | 105 | 10 | 20 | 18 |
| K | 20,900 | – | – | 850 | 518 | 1,100 | 650 |

*Composite samples VA-VIIA also included in the study, were invalidated due to foaming that exceeded the volume of the sample container upon addition of acids to the samples. Foaming due to presence of $CaCO_3$ in the sediments.

Table 12. Comparison of Sediment Sample Matrix for Standard Reference Sediments A and B and MAFLA BLM Sediments. MAFLA data shown is for Group A composite samples. All concentrations are given in ppm on a dry weight basis.

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| Metal | $I_B$ | $II_B$ | $III_B$ | $IV_B$ | $V_B$ | $VI_B$ | $VIII_B$ |
|---|---|---|---|---|---|---|---|
| | | | MAFLA Composite Group B Sediment Samples * | | | | |
| Al | 5,000 | 12,690 | 2,900 | 5,950 | 2,445 | 2,070 | 5,825 |
| Ca | 129,680 | 226,100 | 233,380 | 203,550 | 237,620 | 164,680 | 168,240 |
| Fe | 5,075 | 9,200 | 4,630 | 6,450 | 3,945 | 14,250 | 6,980 |
| Mg | 20,300 | 39,000 | 35,240 | 25,335 | 27,975 | 142,750 | 28,755 |
| Na | 3,515 | 3,865 | 3,820 | 4,615 | 3,765 | 3,600 | 3,735 |
| Si | 162 | 132 | 167 | 165 | 123 | 663 | 207 |

*Potassium content was not measured for this set since KCl was added to control
ionization for calcium and barium.

Table 13.  Results of Matrix Determination of MAFLA BLM Sediments - Group B Composites.
All concentrations are given in ppm on a dry weight basis.

a. $I_A$ and $VI_B$ are highest in magnesium content of set A and set B respectively.

b. $I_A$ and $VI_B$ are highest in silicon.

c. Calcium content of $I_A$ and $VI_B$ is below the average value for each set of composites.

d. $II_A$ and $II_B$ are highest in aluminum content.

e. $I_A$ and $VI_B$ are highest in iron.

f. Sodium concentration averages 3845 ppm for set A and 5636 for set B.

Since the three set A composites were lost during the analysis phase, some patterns may not be obvious. The similarity of composite $I_A$ and $VI_B$ is real: Sample 2-2 is the only sample common to these two composites. The trace metal composition of Sample 2-2 is also likely to differ significantly from the other sediments. The physical appearance of the dried sample is noticeably lighter in color than the other samples.

3. Trace Metal Analysis

The MAFLA sediment composite samples were analyzed for each of the eight metals of environmental interest in the BLM Baseline Survey. The trace metal content of the composite was determined to provide two important pieces of information:

1. Verification that the amount of sample ($\sim$4 gms) and final dilution volume (50 ml) was adequate for necessary minimum detection limit for the MAFLA area sediments; and

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2. Comparison of the concentration values obtained with aqueous

   standards versus matrix-matched standards.

The matrix-matched standards contained aluminum and iron in amounts approximating the average concentration present in the acid digests of the sample. The prepared standards contained 500 ppm aluminum and 1000 ppm iron corresponding to 5000 ppm and 10,000 ppm in the samples respectively. The calcium was added in the form of $CaCl_2$ to make a solution concentration of 20,000 ppm corresponding to 20 percent calcium in the sample.

The observed differences in trace content calculated by comparing the measured sample absorbances with the two sets of standards were significant (Table 14). The smallest difference in trace metal content was noted for nickel (Table 15). Chromium, copper, and vanadium exhibited equivalent differences while lead content was approximately 25% higher when matrix-matched standards were employed. The greatest change of concentration calculated is that for barium; the average concentration of barium calculated with aqueous standards is 348% of the value obtained with matrix-matched standards. The minimum detection limit of cadmium (0.2 ppm) was exceeded by direct flame AAS analysis; no quantitative measurements of cadmium content in the composites were made. The standard curves, both aqueous and matrix-matched, are presented in Figures 13-18. The matrix was matched only for average calcium, iron and aluminum content in the composites so no attempt was made to produce an identical matrix

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| Composite Sample | Cr | | Pb | | Cu | | Ni | | V | | Ba | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Aq | MM | Aq | MM | Aq | MM | Aq | MM | Aq | MM | Aq | MM |
| $I_A$ | 19.63 | 16.52 | 5.78 | 9.70 | 2.89 | 4.16 | 66.42 | 67.81 | 14.09 | 12.01 | 13.63 | 3.93 |
| $III_A$ | 17.04 | 14.24 | 5.83 | 7.01 | 3.45 | 3.88 | 5.50 | 5.61 | 16.18 | 13.92 | 27.73 | 6.90 |
| $IV_A$ | 14.93 | 12.47 | 6.20 | 7.46 | 3.14 | 3.54 | 4.42 | 4.52 | 16.70 | 14.34 | 16.50 | 5.11 |
| $I_B$ | 11.57 | 9.74 | 4.06 | 5.07 | 2.43 | 2.84 | 3.04 | 3.25 | 16.85 | 14.41 | 14.61 | 3.86 |
| $II_B$ | 16.72 | 14.08 | 3.96 | 5.06 | 24.63 | 27.94 | 4.62 | 4.84 | 43.11 | 36.95 | 28.38 | 9.02 |
| $III_B$ | 13.20 | 11.10 | 5.87 | 7.12 | 3.14 | 3.56 | 1.47 | 1.47 | 16.13 | 13.83 | 16.76 | 4.61 |
| $IV_B$ | 18.16 | 15.27 | 8.05 | 9.70 | 4.54 | 5.16 | 5.37 | 5.37 | 18.99 | 16.31 | 18.99 | 5.37 |
| $V_B$ | 14.15 | 11.90 | 6.36 | 7.59 | 3.49 | 3.90 | <D.L. | <D.L. | 15.59 | 13.33 | 17.85 | 5.33 |
| $VI_B$ | 19.69 | 16.37 | 9.74 | 11.81 | 3.52 | 3.94 | 46.43 | 47.47 | 10.57 | 9.12 | 15.55 | 4.56 |
| $VII_B$ | 17.01 | 14.31 | 10.78 | 13.07 | 4.56 | 4.56 | 4.36 | 5.19 | 17.42 | 14.93 | 18.46 | 5.39 |

*D.L. = Detection Limit (sample as opposed to instrumental detection limit).

Table 14. Comparison of Trace Metal Content of Composite MAFLA Sediment Samples for Aqueous (Aq) and Matrix-Matched (MM) Calibration Standards. All results in ppm on a dry weight basis.

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| Trace Metal | Mean Conc: Aqueous Standards Calibration | Mean Conc: Matrix-Matched Standards Calibration | % Net Change* |
|---|---|---|---|
| Cr | 16.21 | 13.60 | - 16.1 |
| Pb | 6.66 | 8.36 | + 25.5 |
| Cu | 3.46† | 3.95* | + 14.2 |
| Ni | 4.11# | 4.32# | + 5.1 |
| V | 18.56 | 15.92 | - 14.2 |
| Ba | 18.85 | 5.41 | - 71.3 |

\* Relative to values obtained via aqueous standards

† Excluding $II_B$

# Excluding $I_A$, $V_B$, $VI_B$

Table 15. Mean Trace Metal Concentrations for MAFLA Composite Sediment Samples as a Function of Aqueous Versus Matrix-Matched Calibration. All results in ppm on a dry weight basis.
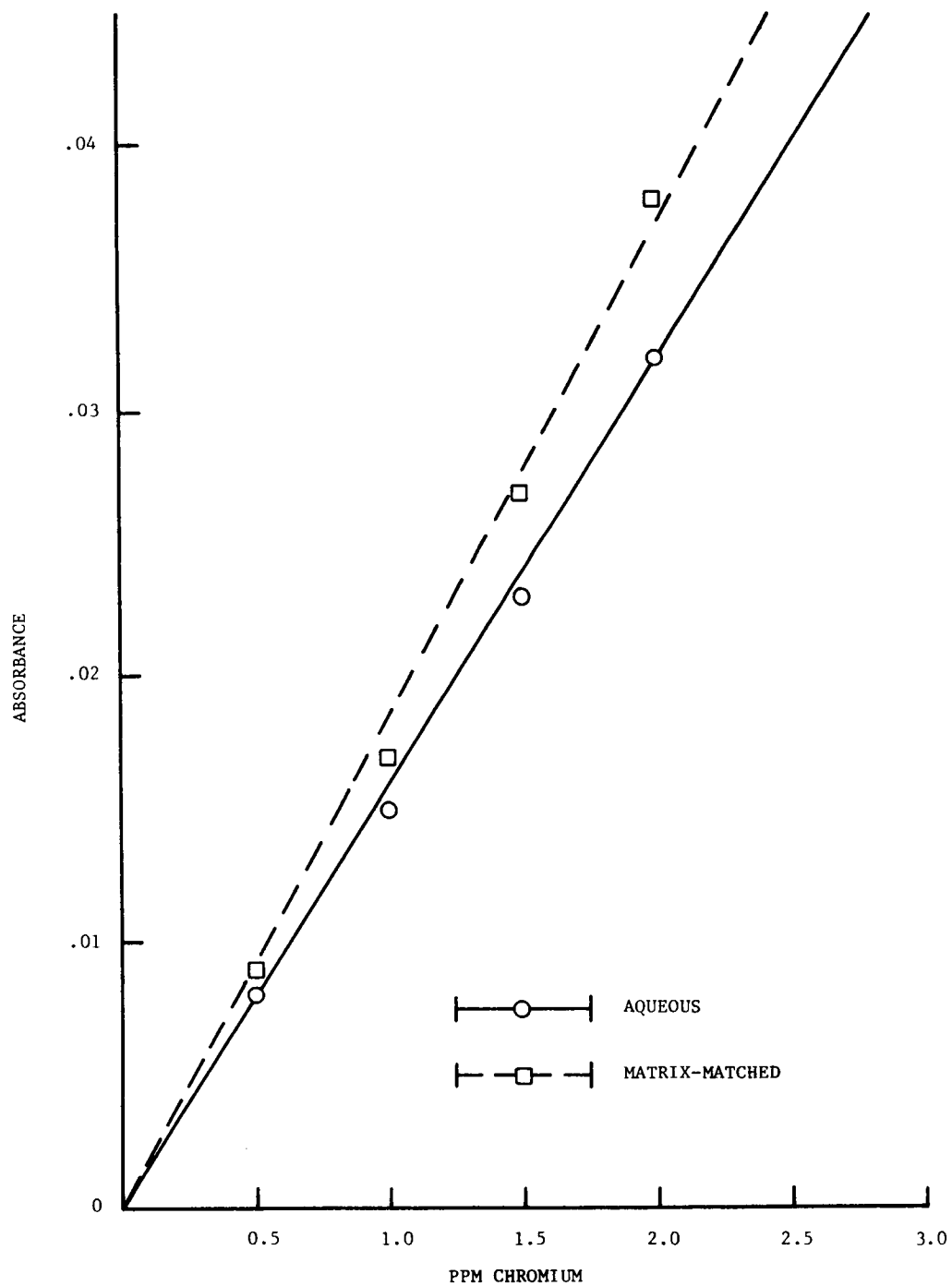
Figure 13. Standard (working) Calibration Curves for Chromium Analysis of MAFLA Sediment
samples. Note matrix effect on chromium (nonparallel lines).

50
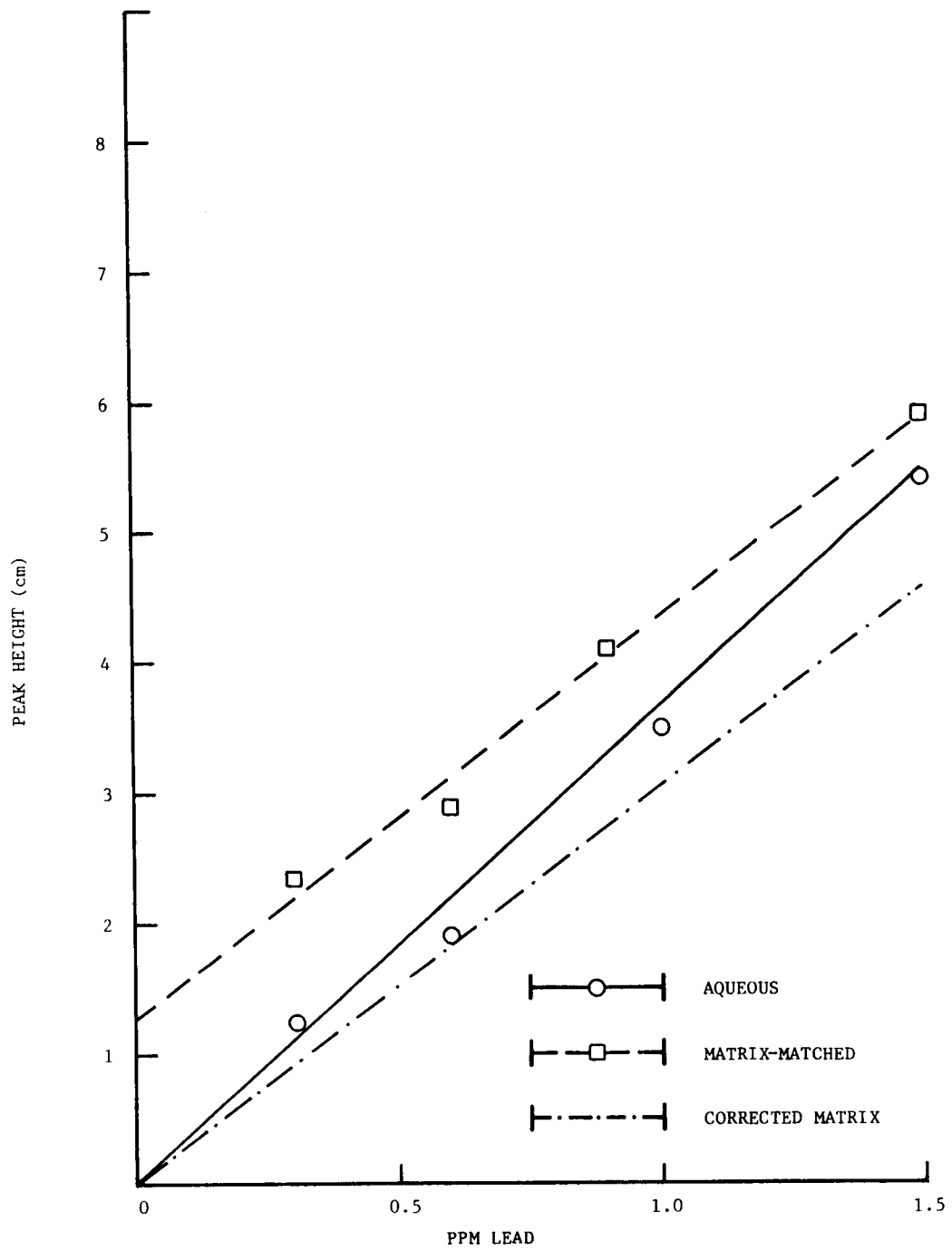
Figure 14. Standard (working) Calibration Curves for Lead Analysis of MAFLA Sediment
Samples. Note matrix effect on lead (nonparallel lines).

51
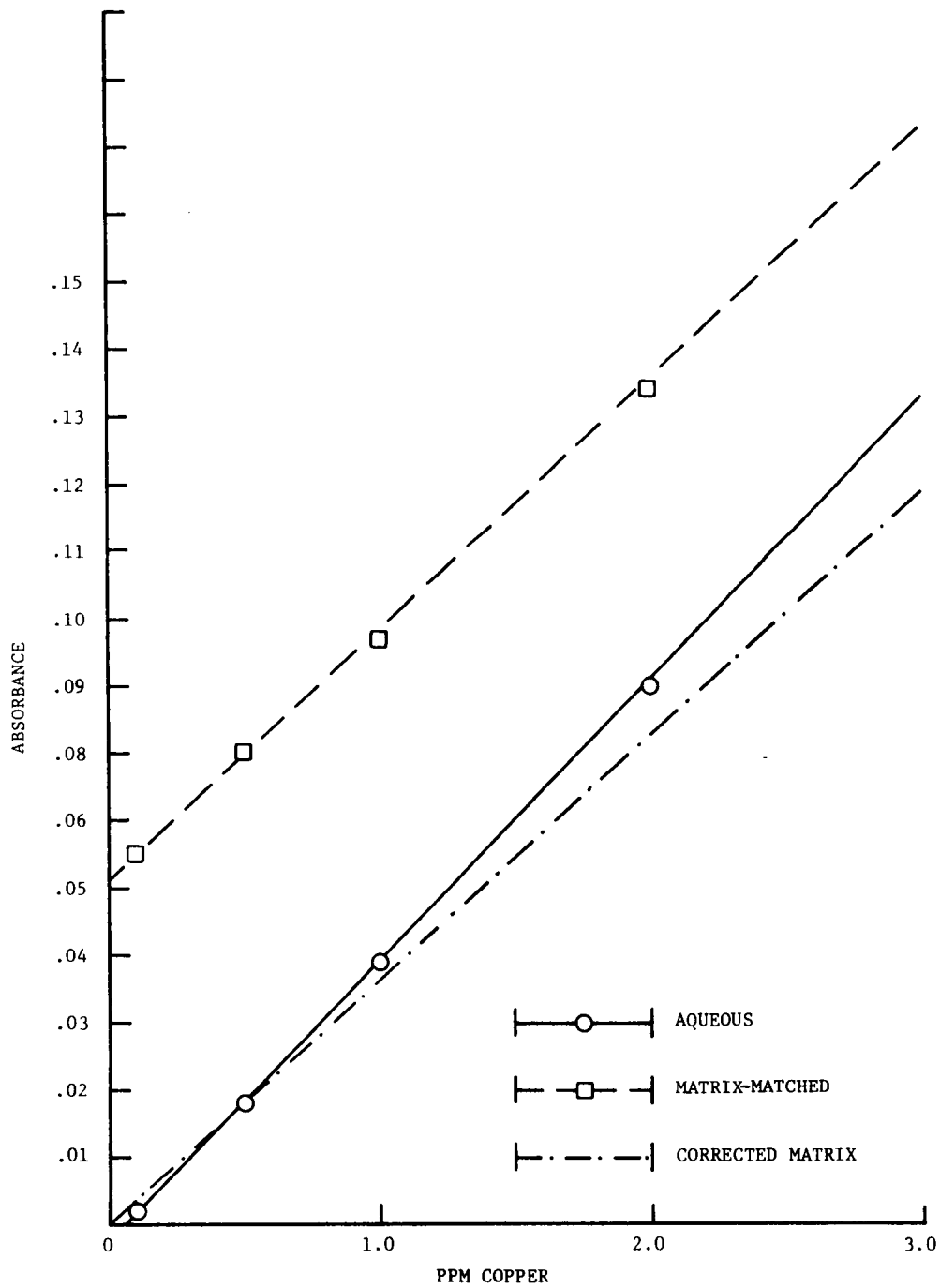
Figure 15. Standard (working) Calibration Curves for Copper Analysis of MAFLA Sediment Samples. Note matrix effect on copper (nonparallel lines).
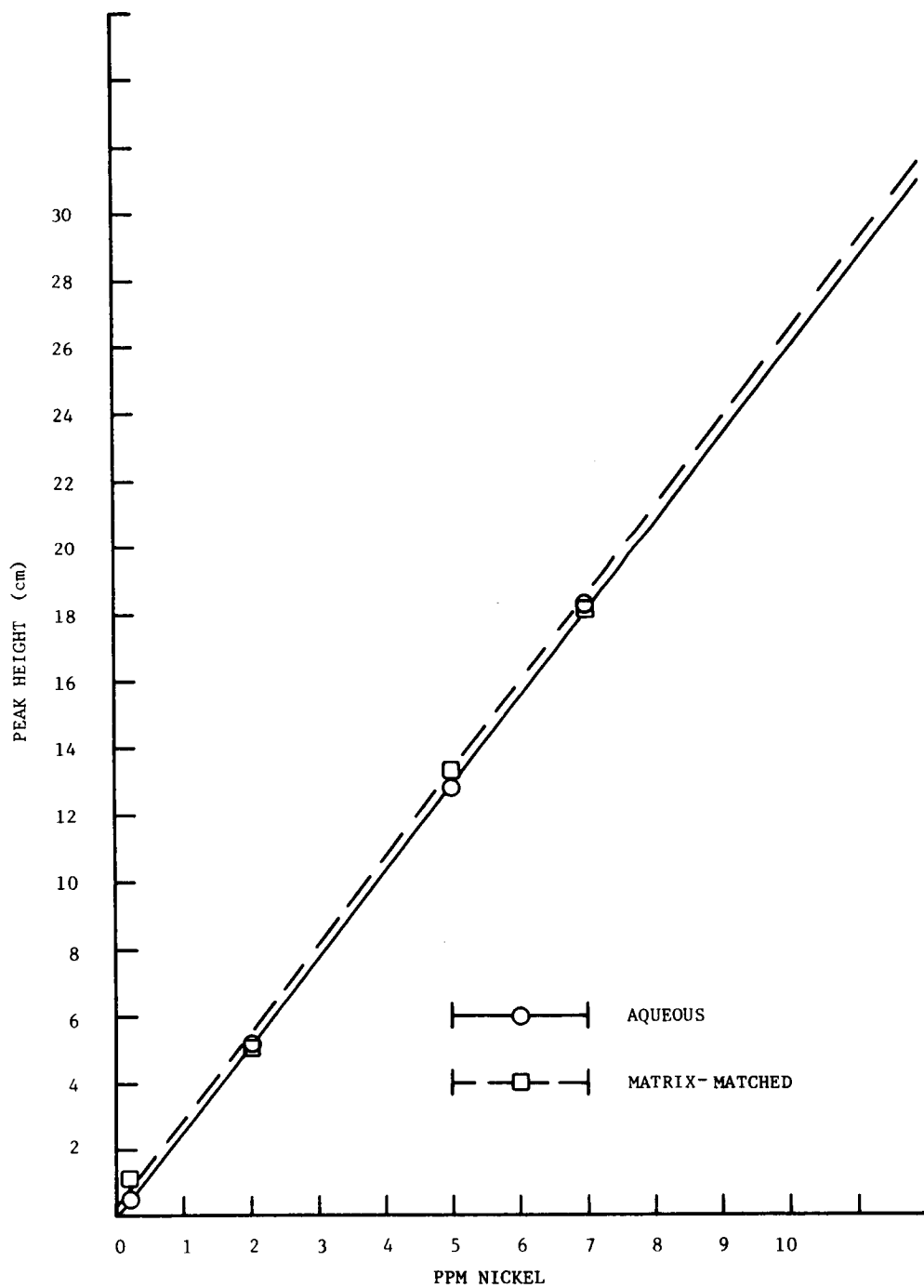
Figure 16. Standard (working) Calibration Curves for Nickel Analysis of MAFLA Sediment Samples. Note apparent lack of matrix effect as evidenced by parallel calibration curves.
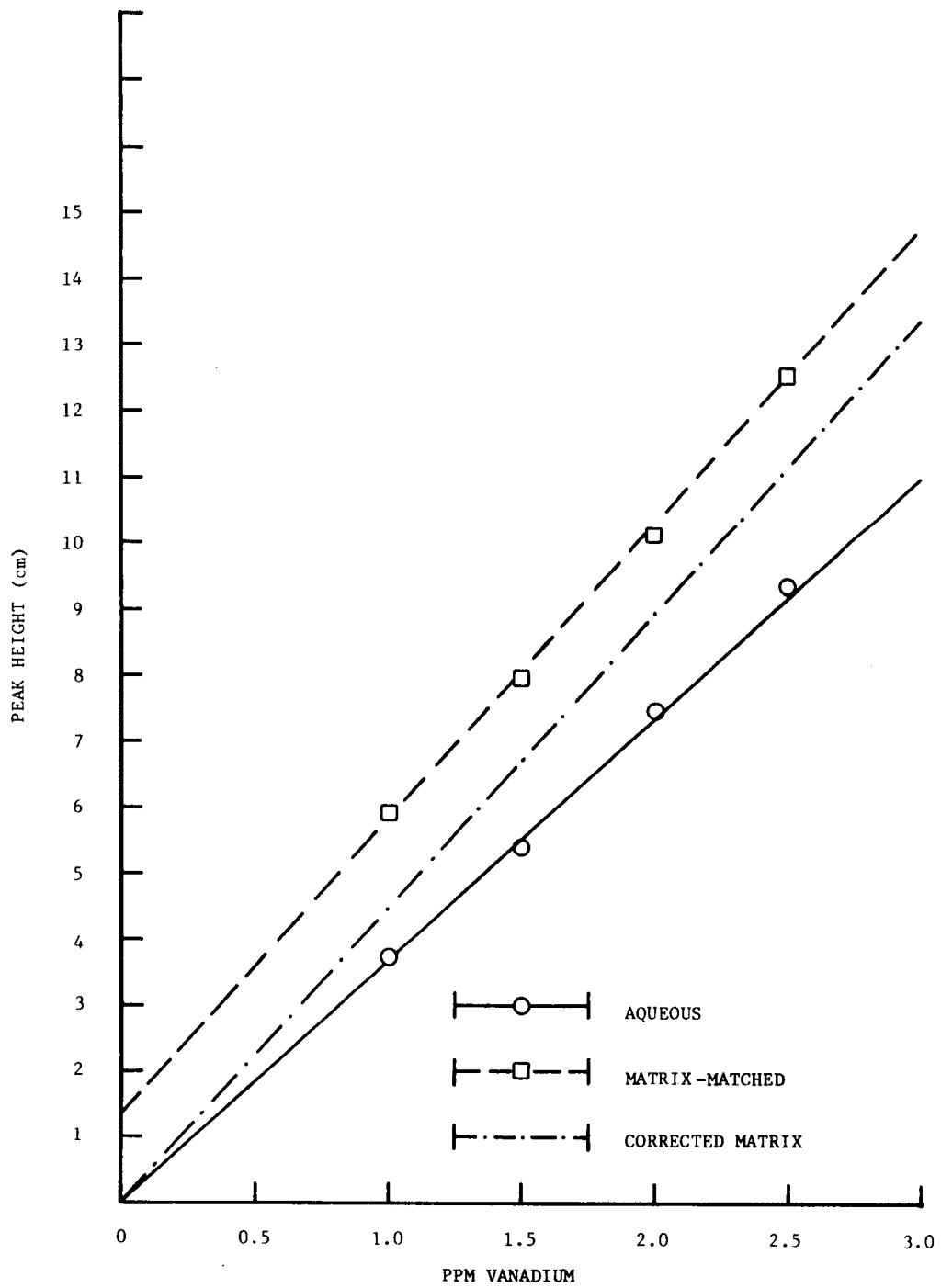
Figure 17. Standard (working) Calibration Curves for Vanadium Analysis of MAFLA Sediment Samples. Note matrix effect on vanadium (nonparallel lines).

54
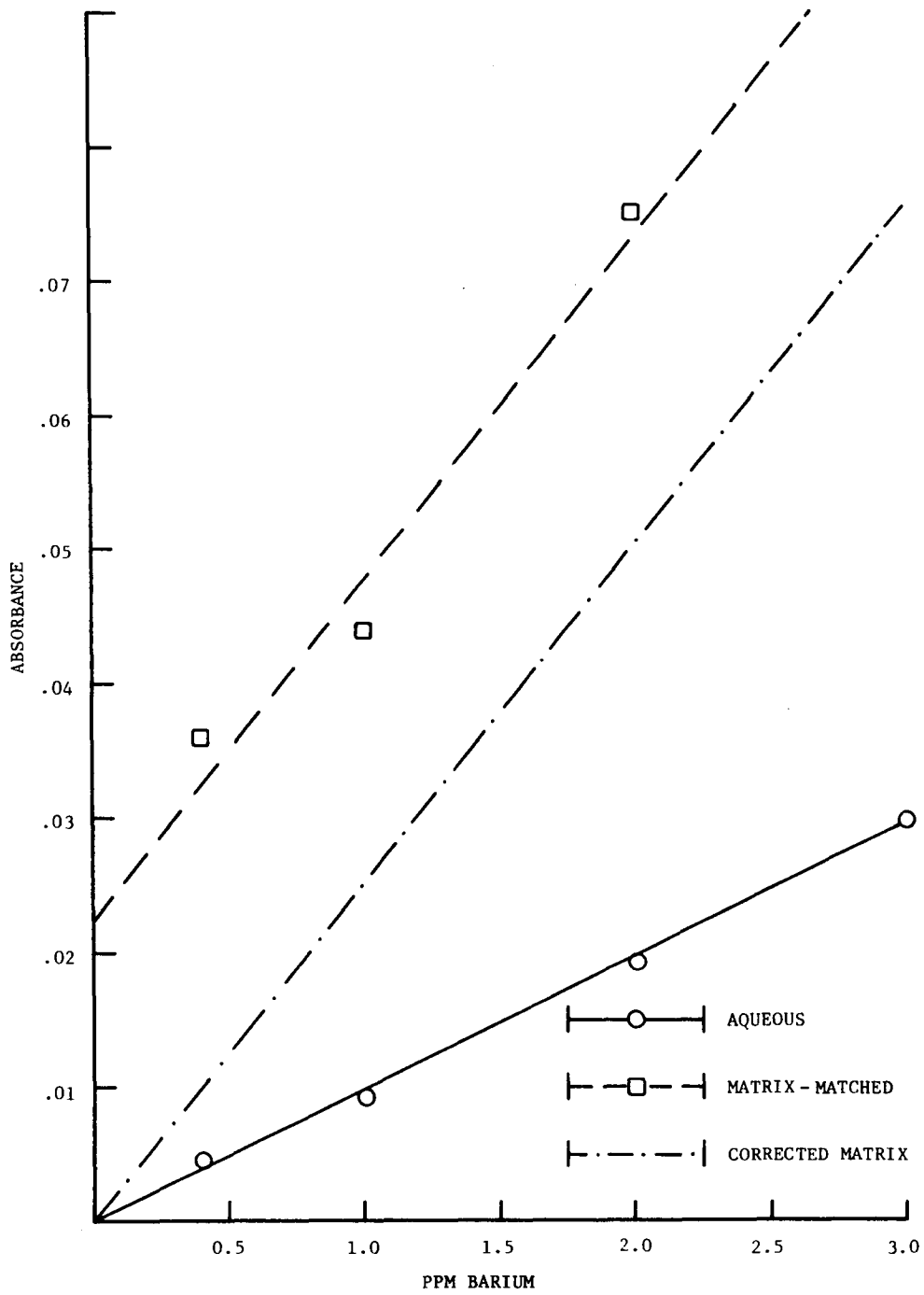
Figure 18. Standard (working) Calibration Curves for Barium Analysis of MAFLA Sediment Samples. Note large matrix effect on barium (nonparallel lines).

in the standards; such a precise match is not feasible since a set

of standards would have to be made for each individual sediment

sample.

Further experimentation was performed for investigation of

potential matrix interferences including more precise matrix-matching.

This data will be described in Chapter III, Sediment Sample Analysis,

since the actual MAFLA sediments were employed.

4. Detection Limit Analysis

The minimum detection limits adopted at this time for trace metal

assay of sediment should be carefully considered. It is important to

note that the minimum detection limit of the Atomic Absorption

Spectrophotometer is not the minimum detection limit for the sediment

sample analysis. Frequently, detection limits are set at levels

several orders of magnitude lower than experimentally feasible.

This section will be devoted to the determination of the detection

limit for the sediment sample; the instrumental detection limits

obtainable in the laboratory with the Perkin-Elmer 306 AAS unit are

listed with other paramaters in Chapter II, Part A.

As a general rule the minimum detection limit is dependent upon

three factors:

1. Instrumental minimum detection limit;

2. Sample size; and

3. Final dilution volume.

The sample size for the analysis of the MAFLA sediments is fixed at

four grams so that duplicate analysis of each sediment is possible. The final dilution volume is chosen such that a sufficient quantity is available for the determination of the required number (8) of elements. The dilution volume chosen for the MAFLA investigation is 50 milliliters. Should the detection limit for several elements be exceeded for a particular group of sediments the dilution volume must be lowered accordingly when the duplicate sets are analyzed.

The instrumental minimum detection limit is of primary consideration here. If the minimum detection limit of the instrument varies, the same variation is inherent in sample analyses. In order to prevent this occurrence the optimization of the instrument prior to analysis is required. The absorbance of a prepared set of standards is (prepared daily from more concentrated or stock solutions) is determined by instrumental setup procedures. The absorbance of a standard of fixed concentration is measured on a day-to-day basis for purposes of optimization. Should the absorbance values previously obtained be higher than the absorbance measured after instrumental setup it is evidence that the AAS is not properly adjusted. If this standard absorbance is exceeded with a particular setup operation then the values used earlier were not measured when the AAS was properly optimized. The use of this quality control check is sometimes neglected due to the adoption of "Concentration Mode" AAS analysis. The reading displayed on the digital printout when the concentration mode is employed is in units of parts per million and is manually adjusted by the operator to read

57.

a particular value. The verification that the instrument is performing

at maximum efficiency is therefore not provided using this method.

The absorbance of a standard may be read prior to switching to the

concentration mode to avoid this occurrence. However, it is

difficult to observe a change in instrumental operation during the

course of an analysis in this mode. Rather than employ this technique,

which is also used for scale expansion purposes, the absorbance mode

is used exclusively in GSRI laboratories. Scale expansion is

obtained by using a strip chart recorder. The calculations are more

time consuming since absorbances must be converted to concentrations.

The trace metal content in the samples must be calculated from the

concentration in solution regardless; one additional step in the

calculation procedure is insignificant when the possibility that

inaccurate results could be obtained more expediently is considered.

A rough estimate of the detection limit (D.L.) for each trace

metal of interest may be provided with the following formula:

$$\text{D.L. (sample)} = \frac{\text{D.L. (instrument)}}{\text{Sample wt. (grams)}} \times \text{dilution factor (ml)}$$

The sample detection limits calculated by this method gave interesting

results (for the case of a four-gram sample size and 50-milliliter

dilution volume). Inspection of the values obtained for the trace

metal assay of the MAFLA composite samples is helpful at this juncture

(Table 14). Detection limits were not exceeded for chromium, lead,

vanadium, or barium with either aqueous standard or matrix-matched

standard calibration. The detection limit for iron will not be

important in this discussion since iron is not a trace metal in these sediments. The D.L. for nickel was exceeded for one sample $(V_B)$ only.

The minimum D.L. was drastically elevated for copper when the matrix-matched standards were used with no contamination correction for calibration of the instrument. Obviously a minimum detection limit of 2-3 parts per million is unacceptable if the values obtained by calibrating with the aqueous standards are to be believed. In order to avoid this pitfall the calibration curve is mathematically shifted to zero intersection. The need for corrected matrix calibration curves arises from trace metals present in chemicals used for matrix-matching. The AA standards employed for preparation of aqueous standards are commercially available in high purity. However, even spectro-grade chemicals and metallic wire contain enough metal in trace amounts to exhibit contamination in atomic absorption measurements. For example, the iron wire employed contributes 1 ppm Cu in the matrix solution. High purity AA standards are commercially available in concentrations of 1000 ppm. In order to obtain a solution more concentrated than 1000 ppm for matrix-matching the use of chemical compounds and/or metallic wire is required. Following mathematical shifting of the matrix calibration curve (the blank is assigned an absorbance of zero) the matrix interference is notable by the lack of parallel relationship between matrix and aqueous curves. The matrix-matched calibration curves used for analysis of trace metal content in the composites were

subjected to zero-intersection corrections (Figures 13-18). These
two types of curves will be included in the discussion of MAFLA Sediment
Sample Analysis (Chapter III).

The instrumental minimum detection limits and the sample minimum
detection limits that were experimentally determined for flame AAS
sediment analyses are listed in Appendix C immediately following the
sediment trace metal data.

The detection limit analysis available for flameless AAS
operation represents the instrumental minimum detection limit. The
sample size and dilution factors were not supplied to GSRI; the
sample detection limit may be calculated by BLM from the instrumental
value if desired. The experimentally determined instrumental
minimum detection limits for flameless AAS analysis are listed in
Appendix C immediately following the seawater trace metal data; these
limits apply also to flameless analysis of suspended particulate
matter and biota extracts (Appendices C and D).

CHAPTER III


TRACE METAL ANALYSIS OF MAFLA SEDIMENT SAMPLES


A.  Sample Preparation

The EPA recommended sediment digestion procedure and GSRI

modifications adopted for the MAFLA sediments are presented in

Appendix A.  The sediments were dried at $103^{\circ}C$ for 24 hours to

assure constant weight.  Approximately eight grams of material

remained following the average matrix determination.  Four grams

of sediment were digested for each sample in duplicate.  Small

letters, a and b, were used to designate duplicate preparations.

The duplicates were not prepared on the same day to eliminate the

possibility that all of a particular sample could be lost during acid

digestion.  The sample weights obtained for both a and b duplicates

are presented in Table 16.  The sediments were analyzed in the

following groupings:

1 a through 7 a

8 a through 28 a

29 a through 35 a; 1 b through 14 b

15 b through 35 b

Only seven sediments were analyzed in the first grouping since the

first set was judged to be most likely out-of-control.  Groups of 20

were subsequently analyzed.  Appropriate quality control checks were

included with each set and are presented in Chapter IV, Quality Control

| BLM SAMPLE I.D. | GSRI SAMPLE I.D. | SAMPLE WEIGHTS (grams) | |
|---|---|---|---|
| | | a | b |
| 1 | 1-1 | 3.9579 | 3.9754 |
| 2 | 2-2 | 4.1636 | 3.9946 |
| 3 | 3-3 | 3.9211 | 3.9303 |
| 5 | 5-4 | 3.9922 | 3.9782 |
| 6 | 6-5 | 3.9841 | 3.9722 |
| 7 | 7-6 | 3.9571 | 3.9555 |
| 9 | 9-7 | 4.0371 | 3.9785 |
| 11 | 11-8 | 3.7779 | 3.9772 |
| 13 | 13-9 | 3.7741 | 3.9608 |
| 16 | 16-10 | 3.8349 | 3.9776 |
| 19 | 19-11 | 3.7909 | 3.9820 |
| 22 | 22-12 | 3.8246 | 3.9532 |
| 24 | 24-13 | 3.7897 | 3.9713 |
| 25 | 25-14 | 3.8046 | 3.9812 |
| 26 | 26-15 | 3.7230 | 4.7740 |
| 27 | 27-16 | 3.7557 | 4.7698 |
| 28 | 28-17 | 3.7957 | 4.5490 |
| 29 | 29-18 | 3.8501 | 4.9618 |
| 30 | 30-19 | 3.8826 | 4.5018 |
| 32 | 32-20 | 3.7893 | 4.6598 |
| 33 | 33-21 | 3.8853 | 4.3814 |
| 34 | 34-22 | 3.8808 | 4.6701 |
| 36 | 36-23 | 3.9080 | 4.5532 |
| 38 | 38-24 | 3.9608 | 4.3299 |
| 39 | 39-25 | 3.7760 | 4.6252 |
| 41 | 41-26 | 3.7943 | 4.5665 |
| 42 | 42-27 | 3.8532 | 4.5450 |
| 44 | 44-28 | 3.8806 | 4.5172 |
| 48 | 48-29 | 3.9715 | 4.3431 |
| 49 | 49-30 | 3.9611 | 4.4163 |
| 54 | 54-31 | 3.9946 | 4.3120 |
| 56 | 56-32 | 3.9794 | 4.0730 |
| 57 | 57-33 | 3.9758 | 4.4674 |
| 60 | 60-34 | 3.9956 | 4.6150 |
| 63 | 63-35 | 3.9751 | 3.4836 |

Table 16. Sample Weights Used for Sediment Analysis of MAFLA Samples. The sediments were dried to a constant weight before the samples were weighed.

section. The components of aqueous and matrix-matched standards used for sediment analysis are in Table 17. The raw data obtained were recorded in a separate laboratory notebook; the peak heights were transferred from the chart recorder paper to this notebook. The charts and raw data will be archived at GSRI until instructions are received for its ultimate disposition.

## B. ANALYSIS DATA

The refined data for analysis of barium, vanadium, cadmium, lead, nickel, copper chromium, and iron present in the 35 sediments is presented in Appendix B. Each trace metal is discussed individually below.

1. Barium

The analysis for barium content was impossible to perform by flame AAS. The analytical wavelength for barium (555 nm) is in the visible region of the spectrum and was subject to flame emission interference from the calcium. The 20% calcium present in the sediments produced a brilliant orange flame in both air-acetylene and nitrous oxide-acetylene flames. The light incident on the photo-multiplier was significant and produced a remarkably noisy analysis. The chart obtained for flame barium analysis is shown in Figure 19. Note the absence of the calcium induced flame emission noise in sample 2 (USGS Standard Rock) previously determined to be calcium-free. The barium analysis was therefore performed by the flameless atomic absorption graphite furnace technique. The flameless technique was not interference-free. The high dissolved solids content of the acid extracts

| Metal | Aqueous Standards (ppm) | | | | Matrix-Matched Standards (ppm) | | | |
|-------|------|------|------|------|-------|-------|-------|-------|
|       | # 1  | # 2  | # 3  | # 4  | # 5*  | # 6*  | # 7*  | # 8*  |
| Cu    | 0.1  | 0.5  | 1.0  | 2.0  | 0.1   | 0.5   | 1.0   | 2.0   |
| Ni    | 0.15 | 0.5  | 1.5  | 3.0  | 0.15  | 0.5   | 1.5   | 3.0   |
| Pb    | 0.3  | 0.6  | 1.0  | 2.0  | 0.3   | 0.6   | 1.0   | 0.2   |
| Cd    | 0.02 | 0.05 | 0.1  | 0.5  | 0.02  | 0.05  | 0.1   | 0.5   |
| V     | 1.0  | 1.5  | 2.0  | 2.5  | 1.0   | 1.5   | 2.0   | 2.5   |
| Ba    | 0.4  | 1.0  | 2.0  | 3.0  | 0.4   | 1.0   | 2.0   | 3.0   |
| Fe    | 0.5  | 1.5  | 3.0  | 5.0  | 0.5   | 1.5   | 3.0   | 5.0   |

Blank     Distilled Water, Reagents, Glassware Matrix Components
          Added to Aqueous Blank

Cd (Flameless)     2.0, 4.0, 6.0, 10.0, 12.0, 14.0, 18.0, 24.0, 28.0 (ppb)

Ba (Flameless)     0.2, 0.4, 0.6, 1.0, 1.4, 2.0, 3.5 (ppm)

* Concentration of Major Constituents (In Standard Solution) Calculated
    from average value measured in sample:

100 ppm K

3000 ppm Mg

400 ppm Na

500 ppm Al

1000 ppm Fe

25000 ppm Ca

Table 17.   Composition of Aqueous and Matrix-Matched Standards Used
            for MAFLA Sediment Analysis.  These standards were used
            for calibration of flame AAS method unless otherwise
            specified.

| SAMPLE | ABSORBANCE RANGE RECORDED |
|--------|---------------------------|
| 1-1a | 0.005 ⟷ 0.015 |
| 2-2a | 0.000 |
| 3-3a | 0.012 ⟷ 0.020 |
| 5-4a | 0.008 ⟷ 0.048 |
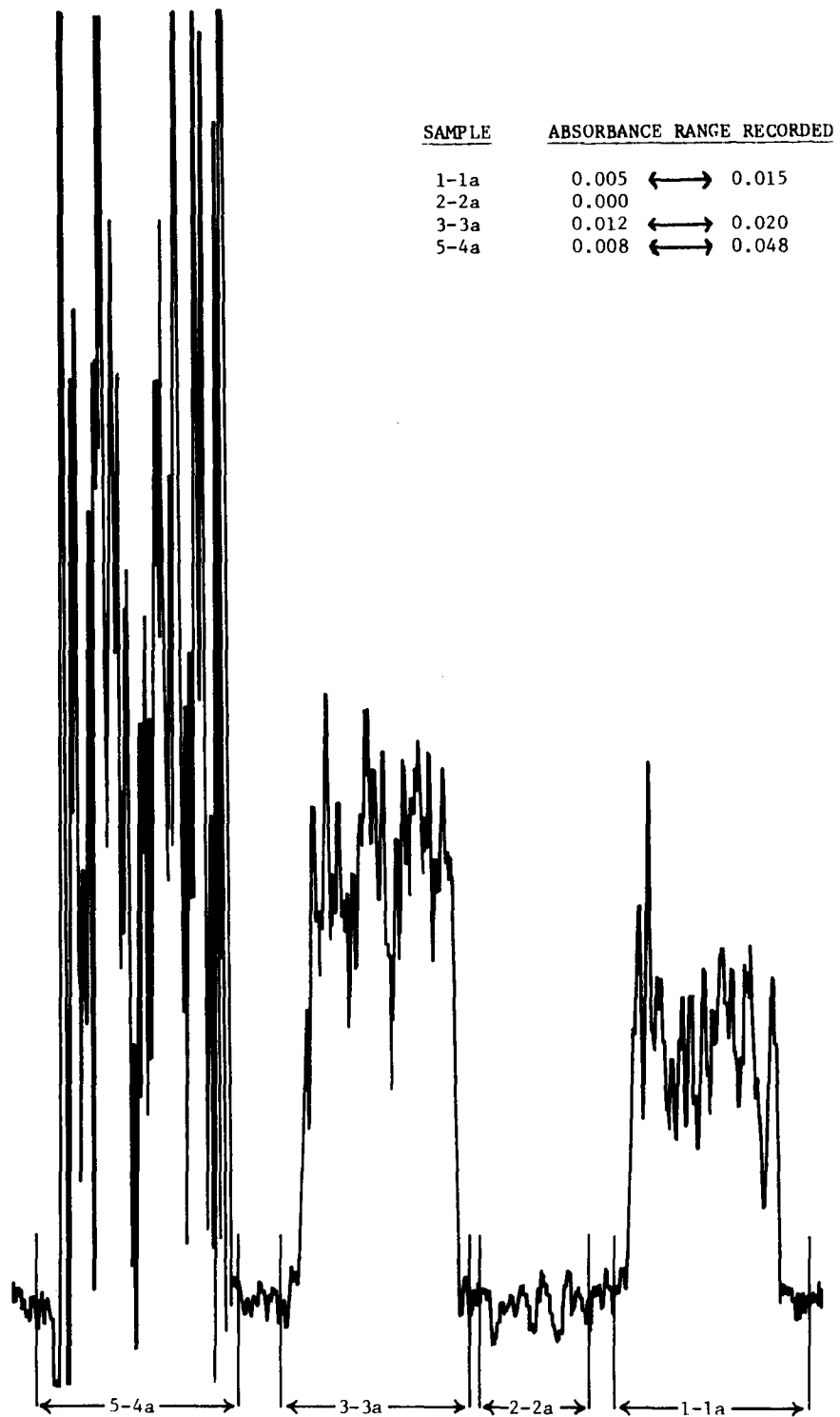
Figure 19. Chart Obtained for Barium Analysis of MAFLA Sediments by Flame AAS. The flame emission noise pattern produced by 20% Calcium is clearly seen for samples 1-1a, 3-3a, and 5-4a.

caused excessive smoking to occur. It was necessary to dry and char the

sample for longer periods of time and atomize at $2600^{o}C$ to eliminate

this interference. As a result some loss of barium occurred during

analysis. The amount of barium lost during dry and char steps was

determined from the percent recovery of spikes obtained (43.2%)

for the SRM's analyzed (Quality Control, Chapter IV). Adjustment of

the barium concentration in the sample was made to correspond to

100% recovery of known spikes. This correction was not ideal since

the SRM's contained no calcium but was preferable to adjustments

made on the basis of aqueous standard losses. The use of

matrix-matched standards was not possible due to the sensitivity

of flameless AAS; the level of contamination in the chemicals used

for matrix-matching for flame AAS exhibited full scale deflection

with flameless AAS. Consequently the data is not available for

barium analysis with both aqueous and matrix-matched standards.

In order to properly analyze for barium by flame AAS the matrix

components contributing to interferent effects must be removed from

the samples via extraction. Alternative sample preparation techniques

such as extraction could not be applied in this case since only ten

grams of sediment were available. This method could, however, be

applied should this problem arise for other geographical areas.

2. Vanadium

The analysis of the sediments for vanadium was easily accomplished

by flame AAS. The sensitivity was adequate for the vanadium

determination. The data is presented in Appendix B for calibration

by both aqueous and matrix-matched standards. A 20% average

difference was observed between values calculated from aqueous versus

matrix-matched standards. The absorbance (peak-height) of the

samples was measured at both the analytical wavelength and at a

nonabsorbing wavelength for vanadium. The analytical wavelength

for vanadium (319.15 nm) is outside the usable range for correction

with the deuterium arc background corrector (200-300 nm). A

nonabsorbing wavelength was selected to measure background absorbance

not otherwise compensated for that might contribute to the vanadium

absorbance. A nonabsorbing wavelength is defined simply as a wave-

length of sufficient intensity for which zero absorbance is obtained

for aqueous standards of the element of interest. It is required

that the nonabsorbing wavelength be ± 2 nm from the analytical line

in order to minimize spectral differences. The source may be a

hollow cathode lamp for any element not present in the sample to

be analyzed. The molybdenum wavelength at 317.8 nm was used for a

vanadium nonabsorbing wavelength. A significant background absorbance

was obtained at 317.8 nm. The vanadium concentration in the sample

was calculated by subtracting the background absorbance from the

absorbance measured at the vanadium analytical line. The correction

ranged from zero (no absorbance at nonabsorbing wavelength) to 528%

(Sample 2) while the average correction was approximately 100%

reduction. A vanadium calibration curve is shown in Figure 20

illustrating the difference between aqueous and matrix-matched

standards. This curve was not employed for calculation of vanadium
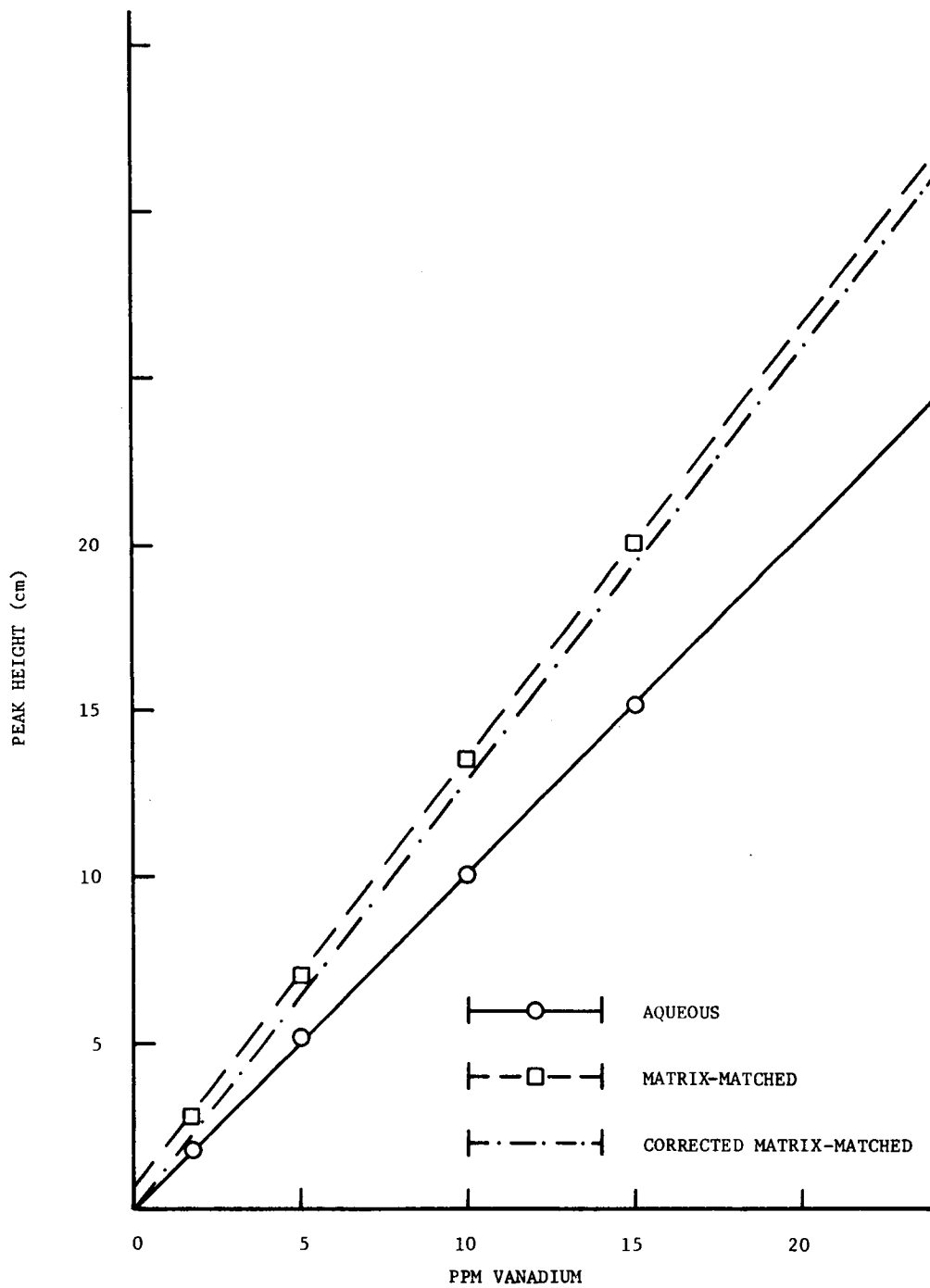
Figure 20. Typical Vanadium Calibration Curves for Aqueous and Matrix-Matched
Standards. The y-intercept of the matrix curve was set equal to zero to obtain
the corrected matrix curve.

content in all 70 cases; the large majority of mathematical manip-

ulations were performed by computer,eliminating the need for

numerous calibrations required for manual computations.

3. Cadmium

The cadmium minimum detection limit by flame AAS (0.2 ppm) was

exceeded necessitating analysis by the flameless graphite furnace

technique. A 25% loss of cadmium was observed during dry and char

steps although 10-second and 20-second intervals were programmed.

As for barium, the percent loss was determined by the average

recovery of cadmium added to the SRM's. The refined data represents

the correction for percent cadmium lost during the flameless analysis.

Matrix-matched standards were not analyzed due to contamination

difficulties maximized by flameless analysis.

4. Lead

Lead content in the sediments was determined by flame AAS.

Comparison of data obtained for aqueous versus matrix-matched

standards illustrated no difference due to the absence of matrix

effect for lead. A calibration curve for lead is shown in Figure 21.

Measurement of absorbance at a nonabsorbing wavelength likewise had

no effect on lead analyses.

5. Nickel

The analysis for nickel content required both a matrix correction

and a nonabsorbing wavelength reading as shown in Figure 22. The

percent difference for aqueous versus matrix-matched calibration was

approximately 10 percent. The absorbance obtained at the nonabsorbing
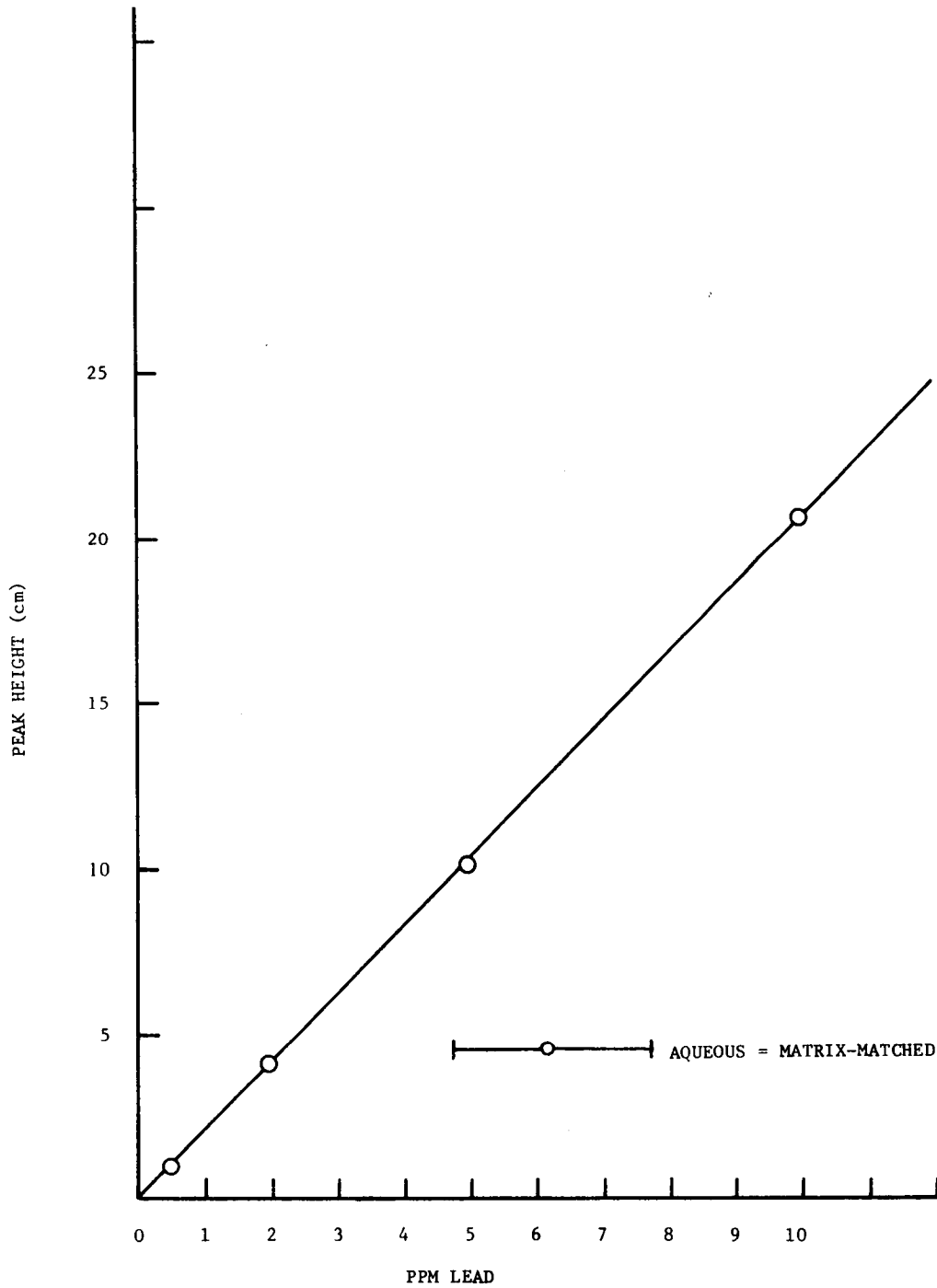
Figure 21. Typical Lead Calibration Curve. Notice that no matrix interference is experienced for lead.

70
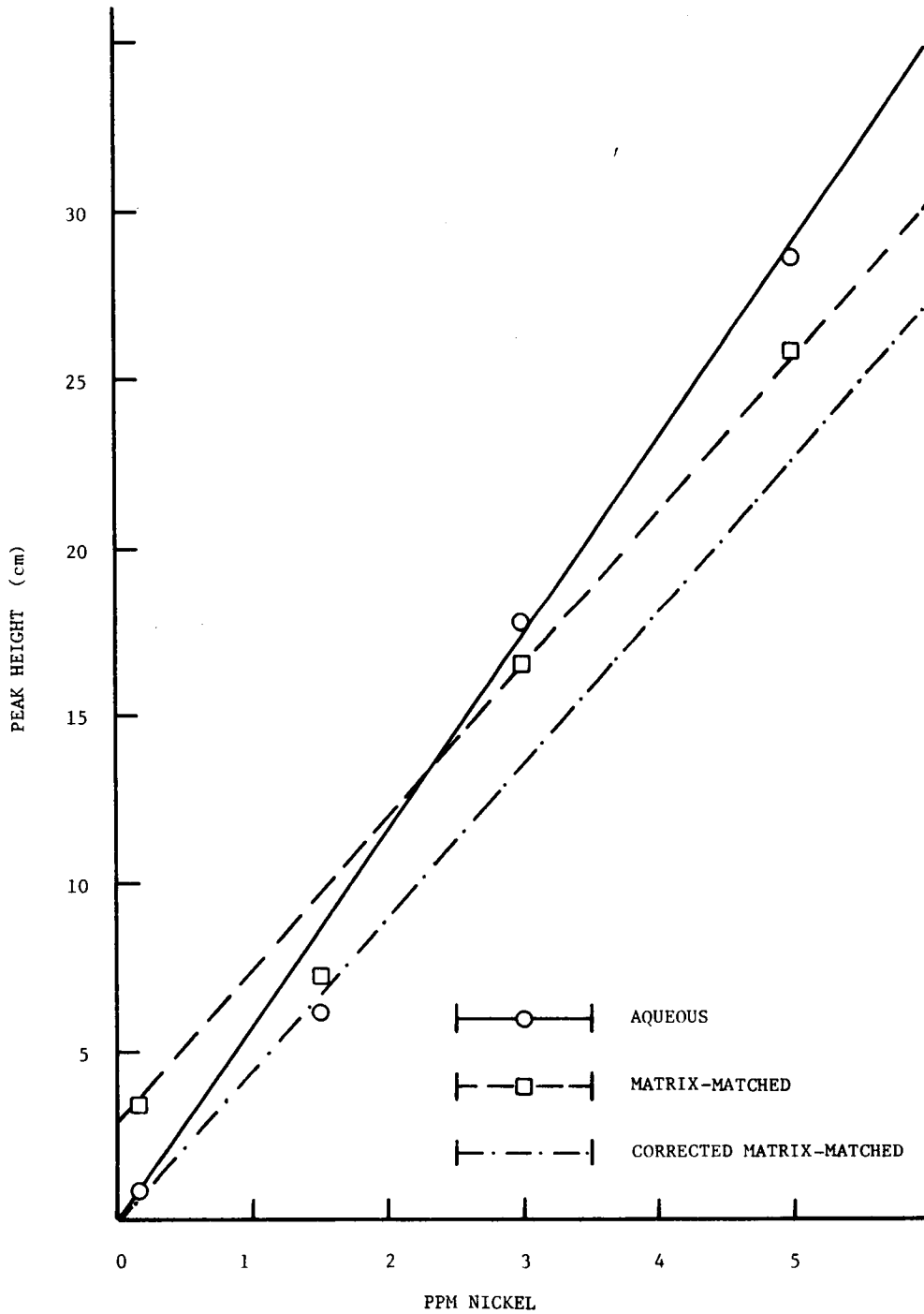
Figure 22. Typical Nickel Calibration Curves for Aqueous and Matrix-Matched Standards. This graph clearly shows the effects of matrix interference on the absorbance of the standards (nonparallel lines).

wavelength (234 nm) was surprising since the analytical nickel line (232.8 nm) is well within the spectral range for optimal correction with the deuterium arc background corrector (200 - 300 nm). The nonabsorbing wavelength provided a 200 - 300 percent correction on the average. The interference responsible for the background absorbance is probably dissolved solids in amounts too high to be automatically subtracted by the deuterium arc system.

6. Copper

The copper determinations required matrix-matching of standards illustrating a 15% - 20% increase in copper compared to aqueous standard calibration. A representative copper calibration curve for both sets of standards is shown in Figure 23. The significant amount of copper contamination in chemicals used for matrix-matching is evident; subtraction of the copper content from each reading still shows a definite matrix interference. The absence of false absorbance was confirmed by monitoring the absorbance at a nonabsorbing wavelength adjacent to the copper analytical line.

7. Chromium

Analysis of the MAFLA sediments for chromium was performed by using aqueous and matrix-matched standards. A matrix effect was noted as illustrated in Figure 24. The minimal chromium contamination in chemicals used for matrix-matching is apparent. The values obtained with matrix-matched standards were 10 percent lower than for aqueous standards. A background absorbance was not exhibited for the corresponding nonabsorbing wavelength measurements.

72
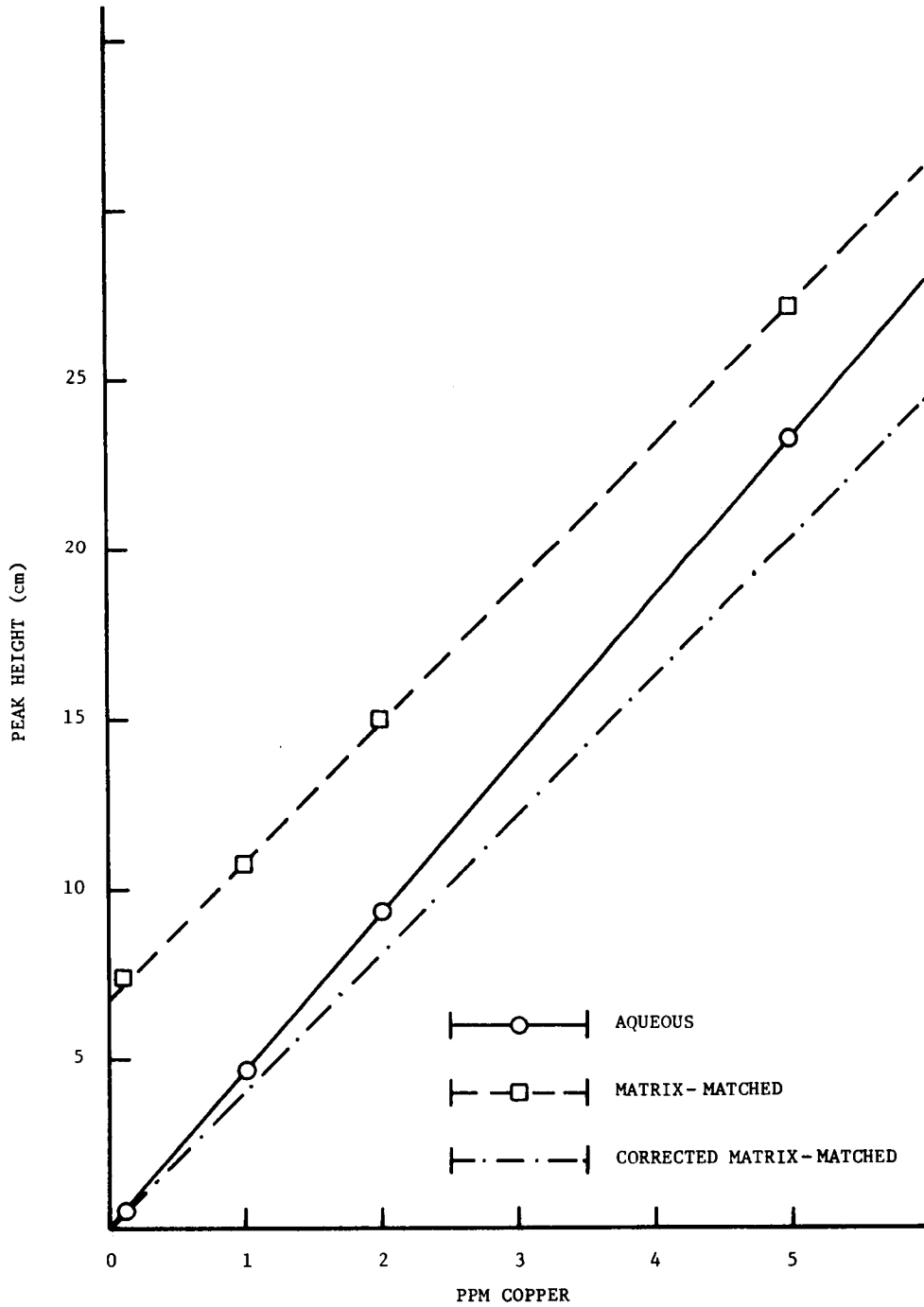
Figure 23. Typical Copper Calibration Curves for Aqueous and Matrix-Matched
Standards. The large y-intercept is due to some copper contamination in the
reagents used to repair the artificial matrix constituents.
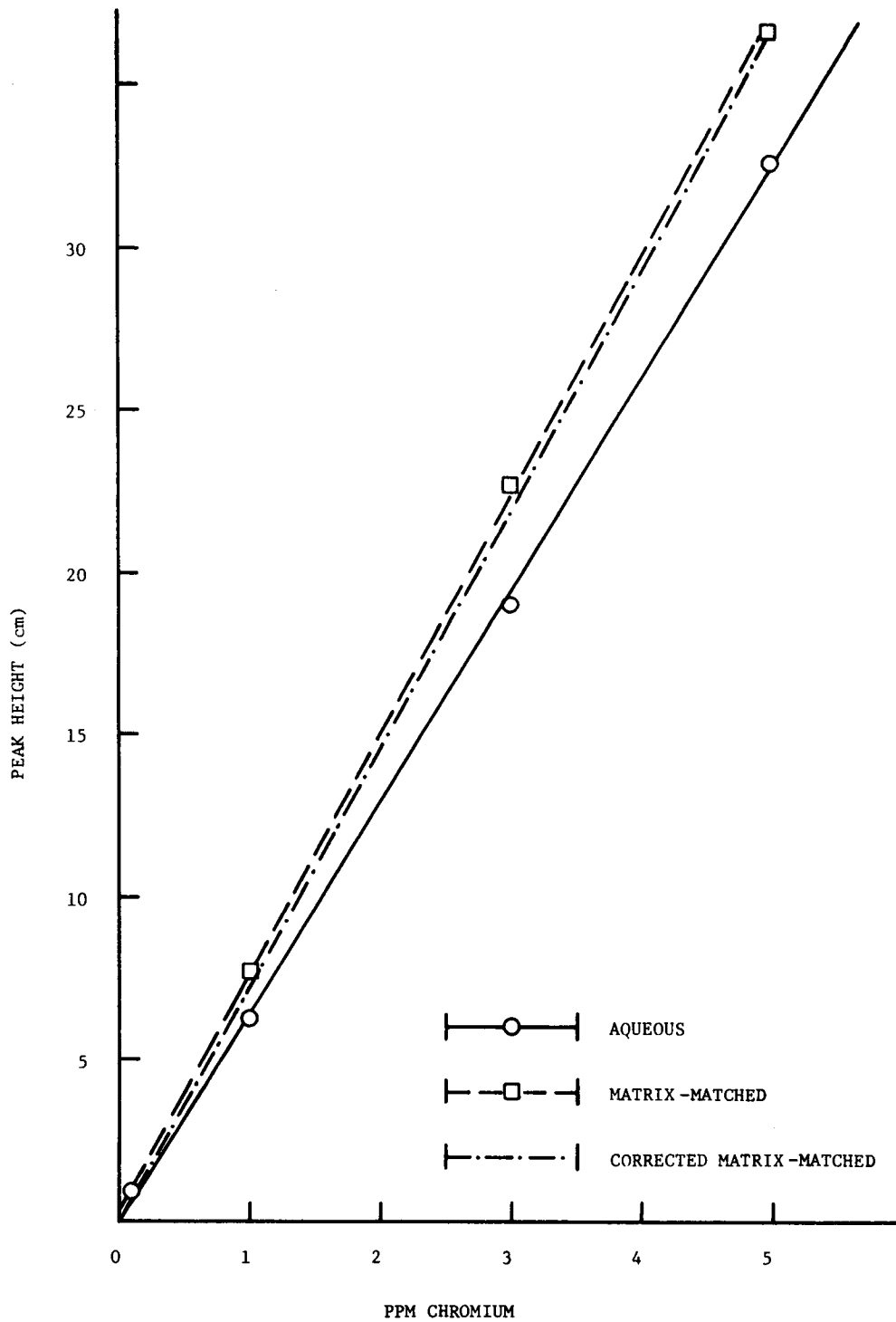
Figure 24. Typical Chromium Calibration Curves for Aqueous and Matrix-Matched
Standards. Note that for chromium the matrix causes an enhancement of
absorbance.

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8.  Iron

   The presence of iron in greater than trace amounts proved to
be the only difficulty encountered for sediment analysis for iron.
A large dilution was necessary in order to utilize the linear
portion of analytical calibration curves.  Results obtained by a
colorimetric method and by flame AAS is presented in Table 18 (31).
The two techniques yielded comparable results.  The analysis of
duplicate samples for BLM samples number 26 and 41 was also in
excellent agreement by both methods.  A matrix effect was not noted
with iron, Figure 25 .

| BLM Sample I.D. | Colorimetric ppm Fe | AAS ppm Fe |
|---|---|---|
| 26-a | 14770 | 14370 |
| 26-b | 13390 | 13310 |
| 27-b | 13420 | 12420 |
| 41-a | 14490 | 12020 |
| 41-b | 14230 | 11880 |

Table 18. Results of Iron Determinations by Colorimetric Versus AAS Analysis Techniques. The colorimetric determination was made by measuring the absorbance of an iron-phenanthroline complex at 510 nm.
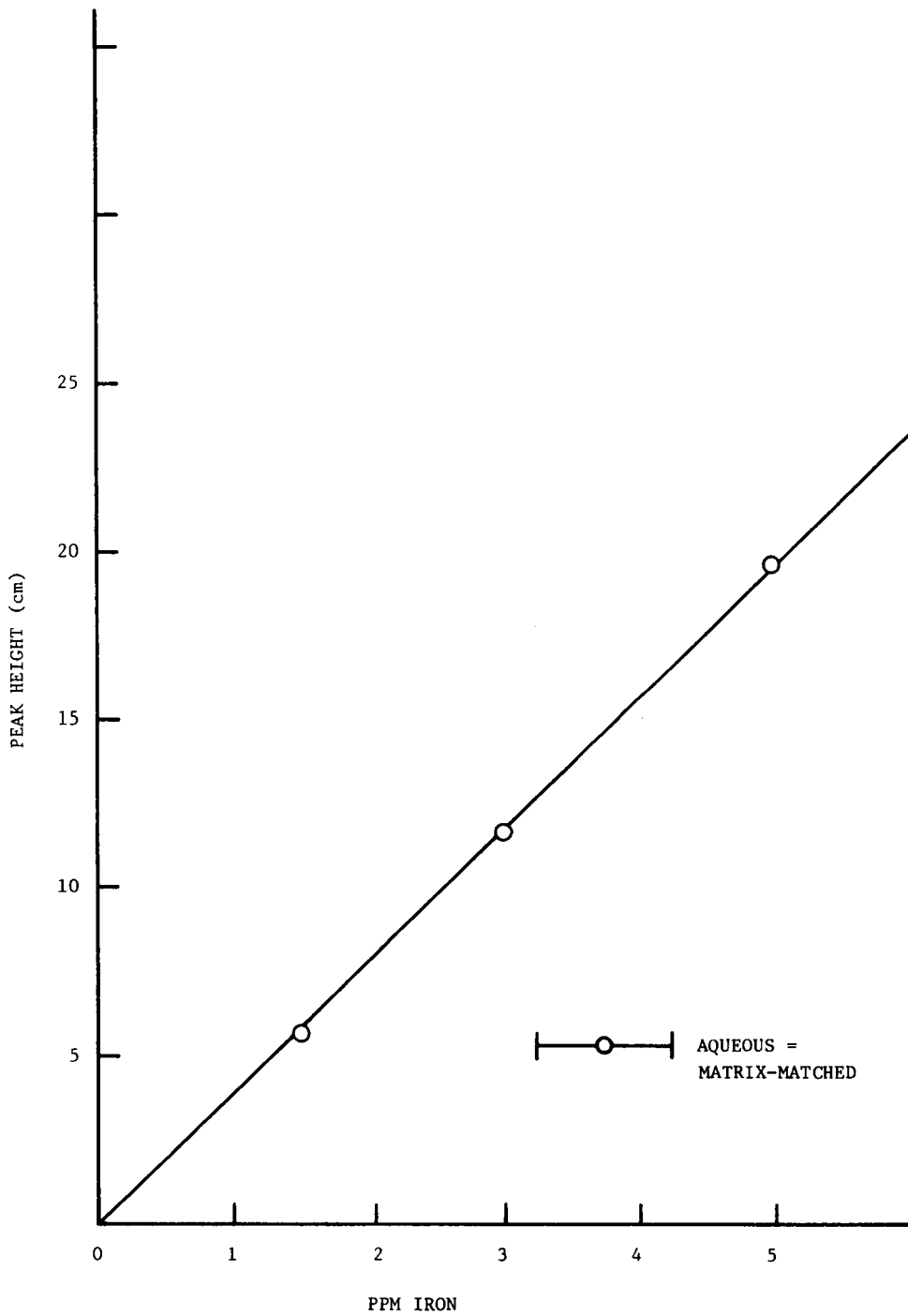
Figure 25. Typical Iron Calibration Curve. Iron is a major matrix constituent and its absorbance is unaffected by the other matrix elements.

CHAPTER IV


QUALITY CONTROL PERFORMED FOR SEDIMENT SAMPLES

A.  Standard Reference Sediments

The two sediment samples, designated A and B, that were
analyzed for investigation of matrix interferences described in
Progress Report I were used as in-house Standard Reference
Materials (SRM) for sediment analysis.  The quantity of trace metal
present in the samples was established by 45-50 replicate analyses
performed by the same procedure as the MAFLA sediments.

A set of SRM's was carried through the digestion procedure with
each set of MAFLA sediments.  Analysis of trace metal content was
performed concurrent with MAFLA sediment determinations.  The SRM
set includes one of Sample A, one spiked Sample A, duplicates for
Sample B, and duplicate spikes for Sample B.  The identification
scheme employed for the SRM sets is presented in Table 19 in addition
to the corresponding MAFLA sediment set.  Spiked samples contained
additions of trace metal in the following concentrations:

<div align="center">

Barium     - 50 ppm

Vanadium   - 50 ppm

Cadmium    - 25 ppm

Lead       - 50 ppm

Nickel     - 50 ppm

</div>

| BLM Sediment Group | Corresponding SRM Group | Comments |
|---|---|---|
| 1a - 7a | A-a | |
| | A-sp-a | sp - spiked sample |
| | B-1-a | |
| | B-2-a | |
| | B-1-sp-a | sp - spiked sample |
| | B-2-sp-a | sp - spiked sample |
| 8a - 28a | A-b | |
| | A-sp-b | sp - spiked sample |
| | B-1-b | |
| | B-2-b | |
| | B-1-sp-b | sp - spiked sample |
| | B-2-sp-b | sp - spiked sample |
| 29a - 35a; | A-c | |
| 1b - 14b | A-sp-c | sp - spiked sample |
| | B-1-c | |
| | B-2-c | |
| | B-1-sp-c | sp - spiked sample |
| | B-2-sp-c | sp - spiked sample |
| 15b - 35b | A-d | |
| | A-sp-d | sp - spiked sample |
| | B-1-d | |
| | B-2-d | |
| | B-1-sp-d | sp - spiked sample |
| | B-2-sp-d | sp - spiked sample |

Table 19. Identification of Standard Reference Materials A and B. The numerals indicate duplicate samples within a group while the lower case letter designates the corresponding BLM sediment grouping.

Copper    - 50 ppm

Chromium  - 50 ppm

The SRM analyses provided four important quality control checks:

1.  The analysis of the unspiked Samples A and B was compared to the previous replicate analyses to determine if the digestion procedure was in-control.

2.  The analysis of the spiked samples and resultant calculation of percent recovery gave information regarding accuracy.

3.  The percent recovery of spikes could be compared for aqueous versus matrix-matched standards thereby indicating if a matrix correction was required.

4.  Analysis of Sample B in duplicate, both spiked and unspiked, provided precision information.

Each of the four quality control considerations will be discussed in detail below.

1.  In-Control versus Out-of-Control.  The median value for each trace metal of interest is represented in Figures 26-32 on transparent overlays over Figures 1 through 7.  The analysis of the SRM samples is included on the overlay and each sample is identified as shown in Table 19.

    a.  Barium

    It was not possible to apply the median values of barium in A and B to in-control versus out-of-control decisions since 60% of the barium was lost during flameless

80
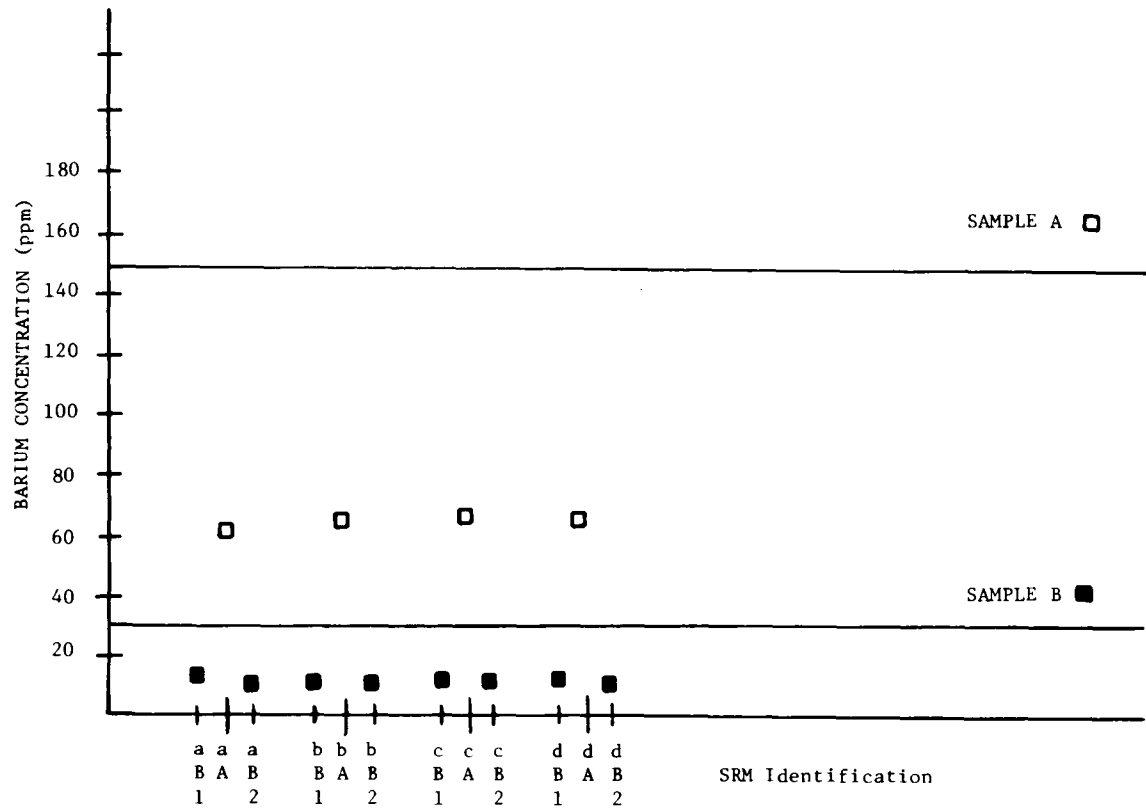
Figure 26. Barium Quality Control Chart. The SRM identification on the x-axis corresponds to that given in Table 19 for unspiked sediments; the solid horizontal lines represent the median barium concentration in Sample A and Sample B obtained from the data on the underlay (Figure 1).
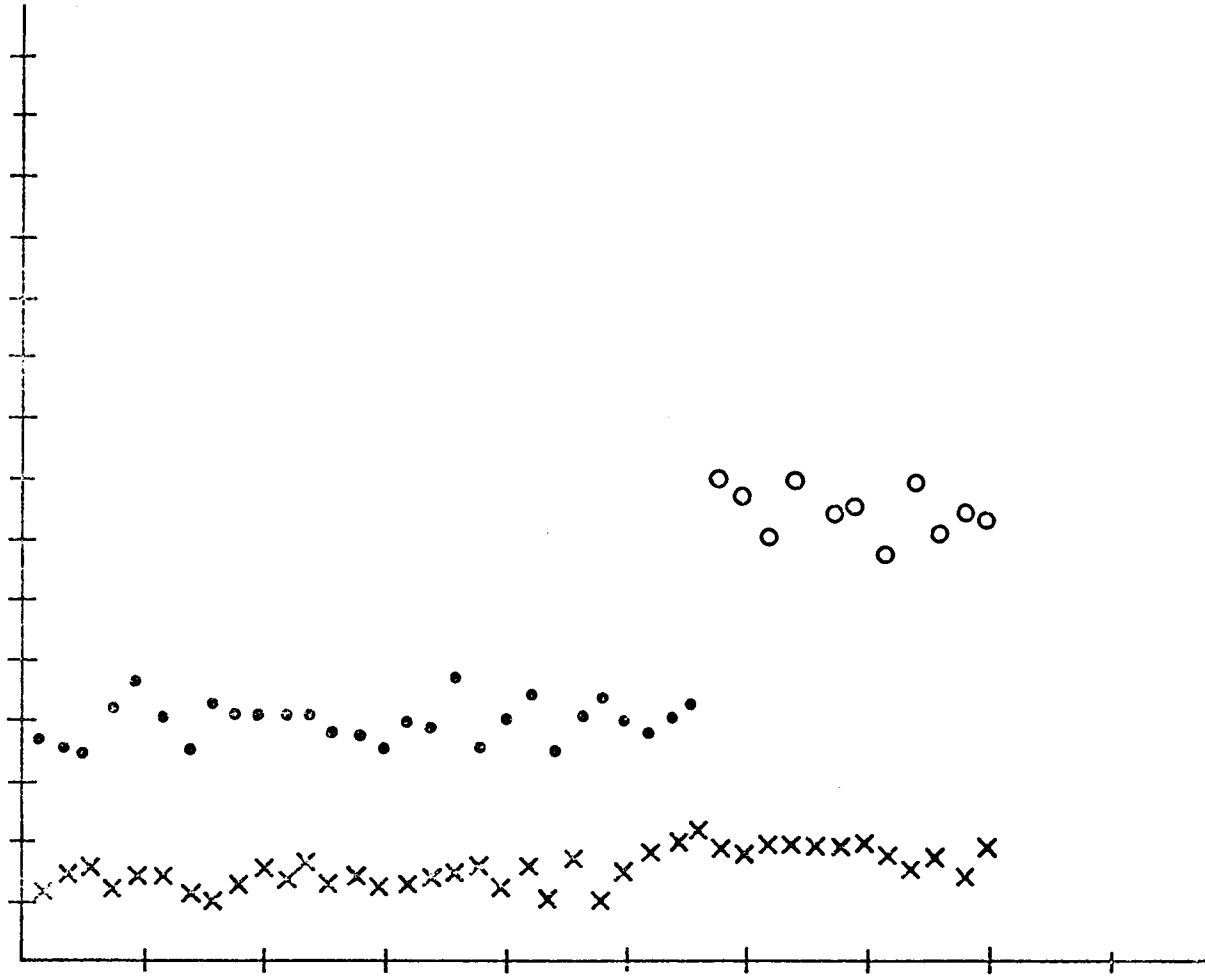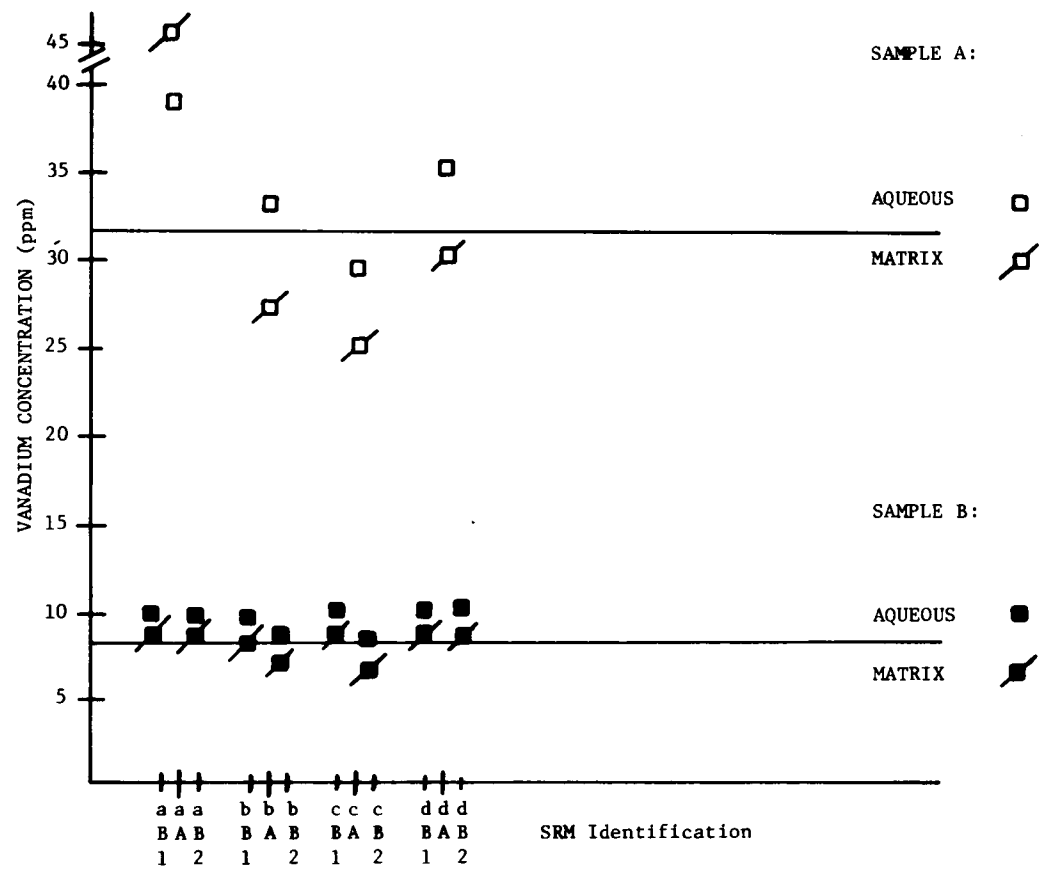
Figure 27. Vanadium Quality Control Chart. The SRM identification on the x-axis corresponds to that given in Table 19 for unspiked sediments; the solid horizontal lines represent the median vanadium concentration in Sample A and Sample B obtained from the data on the underlay (Figure 2).

CADMIUM CONCENTRATION (ppm)

SAMPLE B:

1.5

FLAMELESS ■

FLAME ◢

1.0

SAMPLE A:

0.5

FLAMELESS ▢

0.375

0.25

0.125

FLAME ▱

a a a    b b b    c c c    d d d
B A B    B A B    B A B    B A B     SRM Identification
1   2     1   2     1   2     1   2
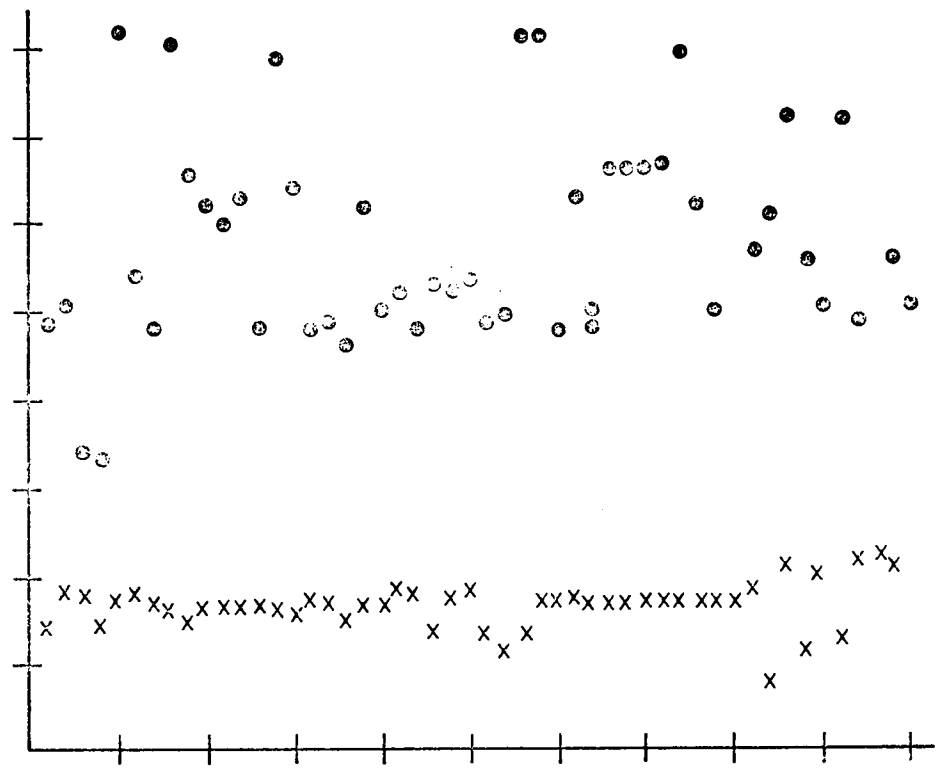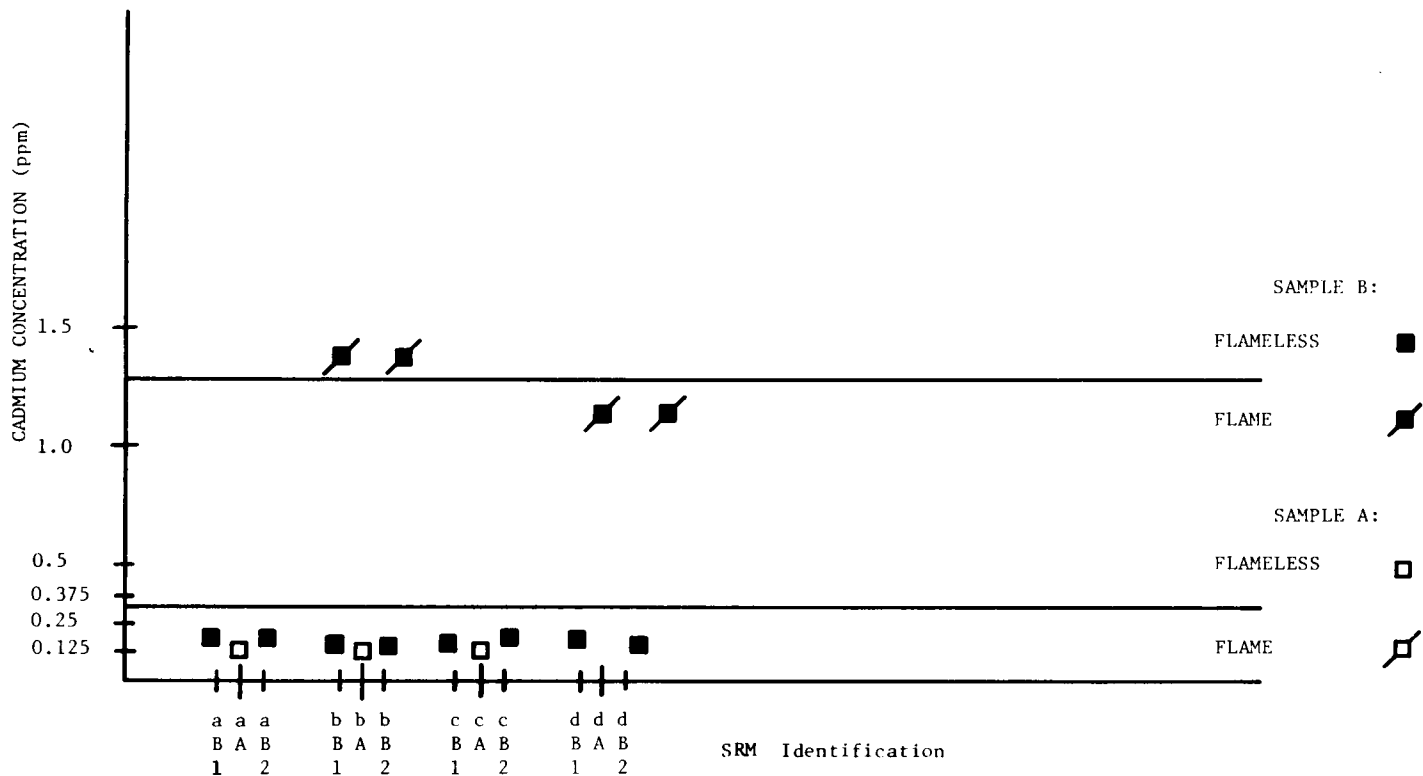
Figure 28. Cadmium Quality Control Chart. The SRM identification on the x-axis corresponds to that
given in Table 19 for unspiked sediments; the solid horizontal lines represent the median cadmium
concentration in Sample A and Sample B obtained from the data on underlay (Figure 3).
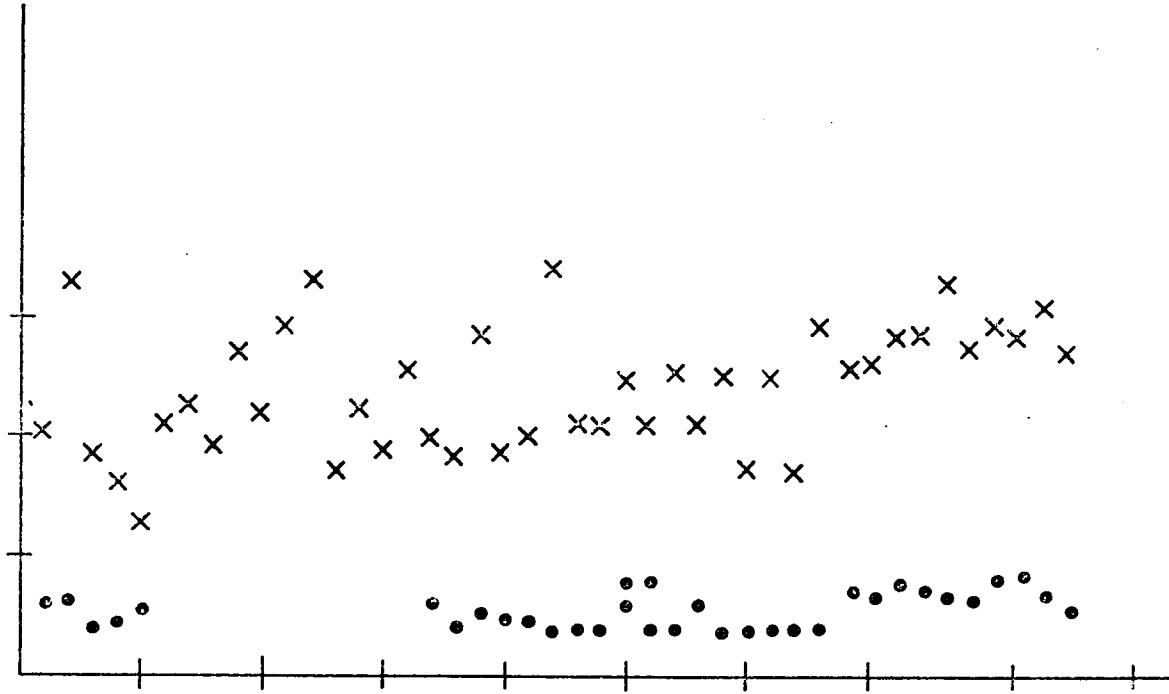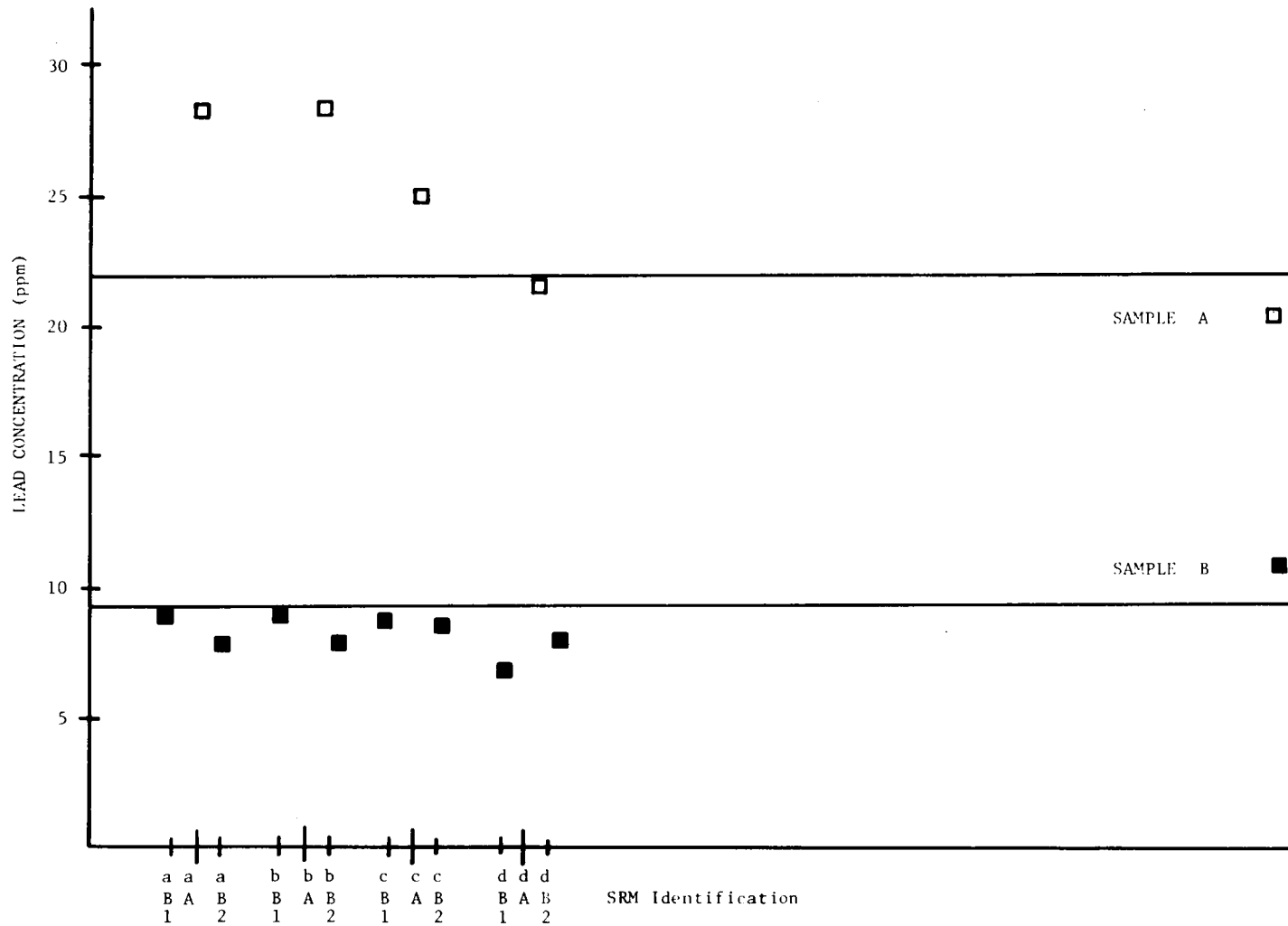
Figure 29. Lead Quality Control Chart. The SRM identification on the x-axis corresponds to that given in Table 19 for unspiked sediments; the solid horizontal lines represent the median lead concentration in Sample A and Sample B obtained from the data on the underlay (Figure 4).
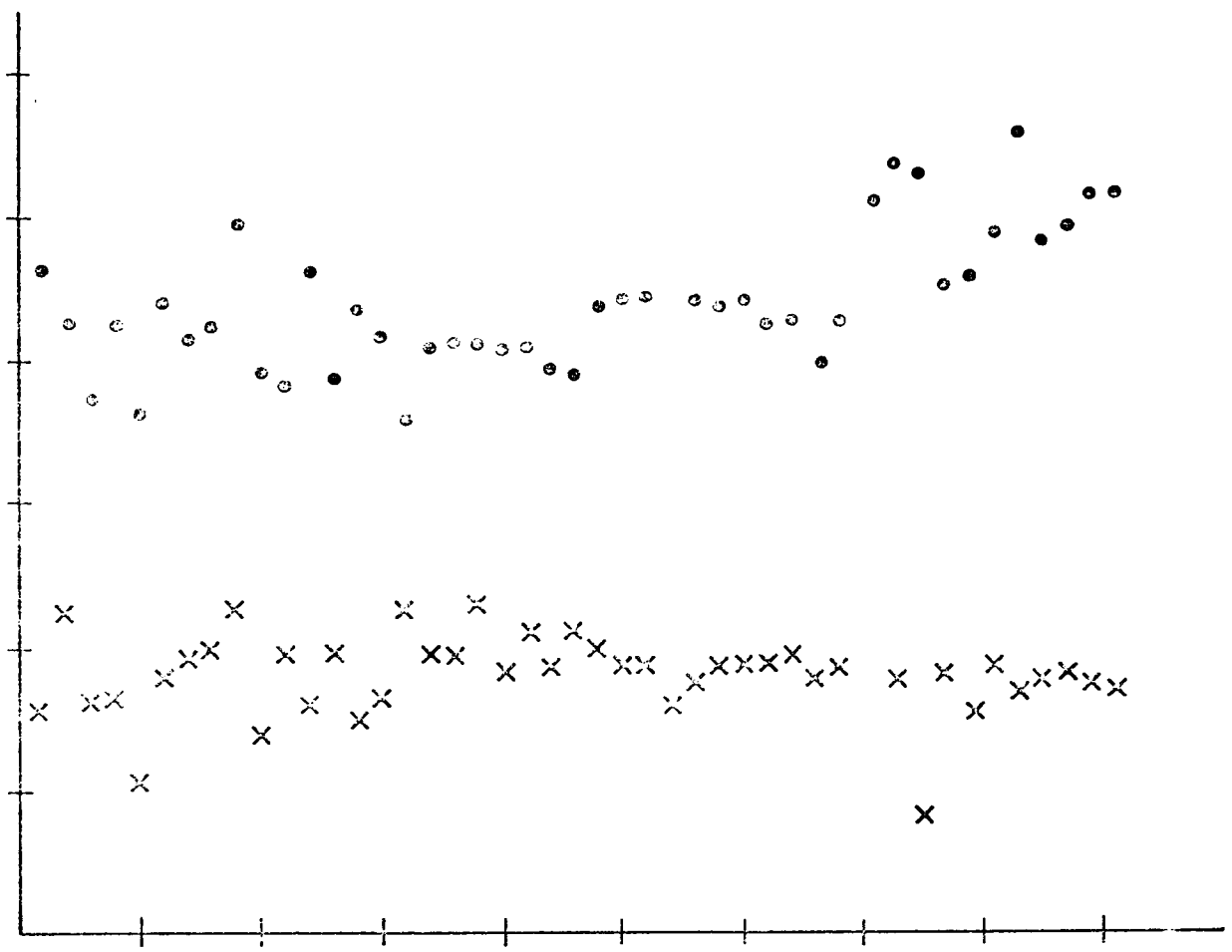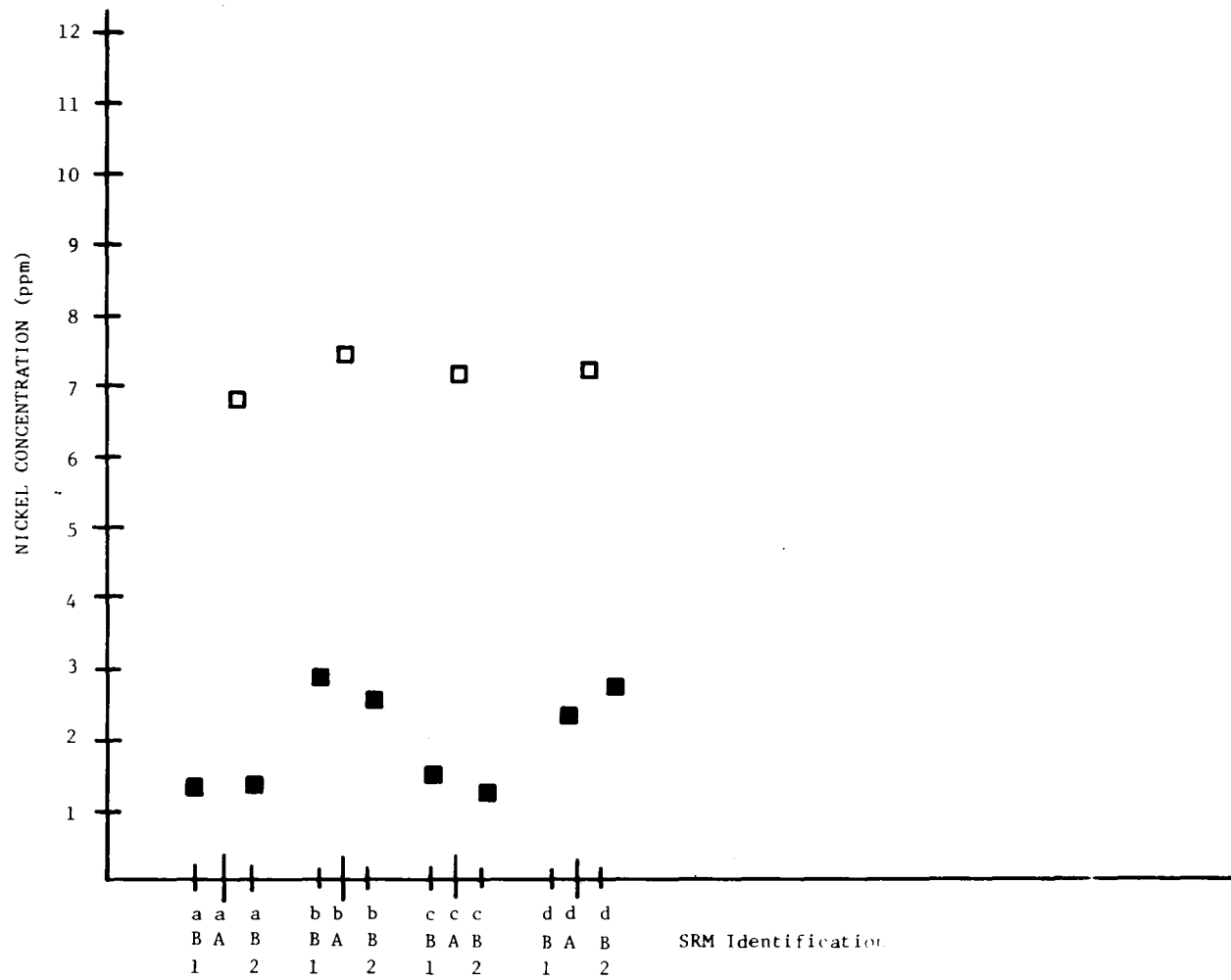
Figure 30. Nickel Quality Control Chart. The SRM identification on the x-axis corresponds to that given in Table 19 for unspiked sediments.
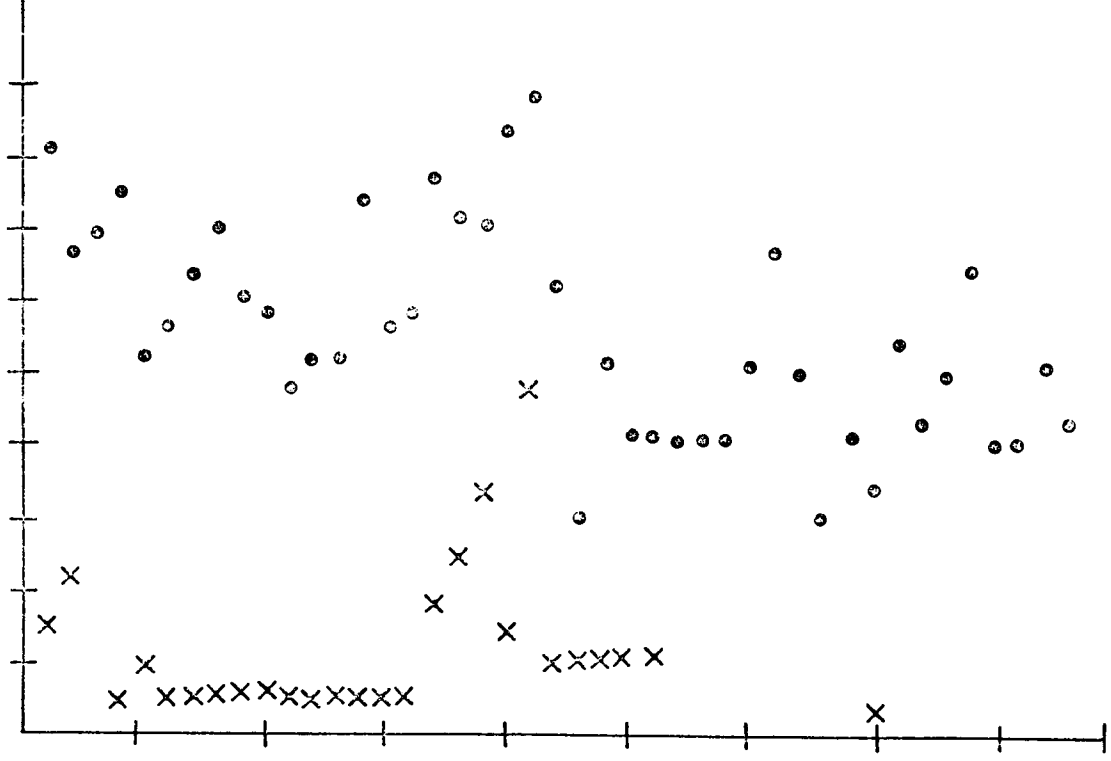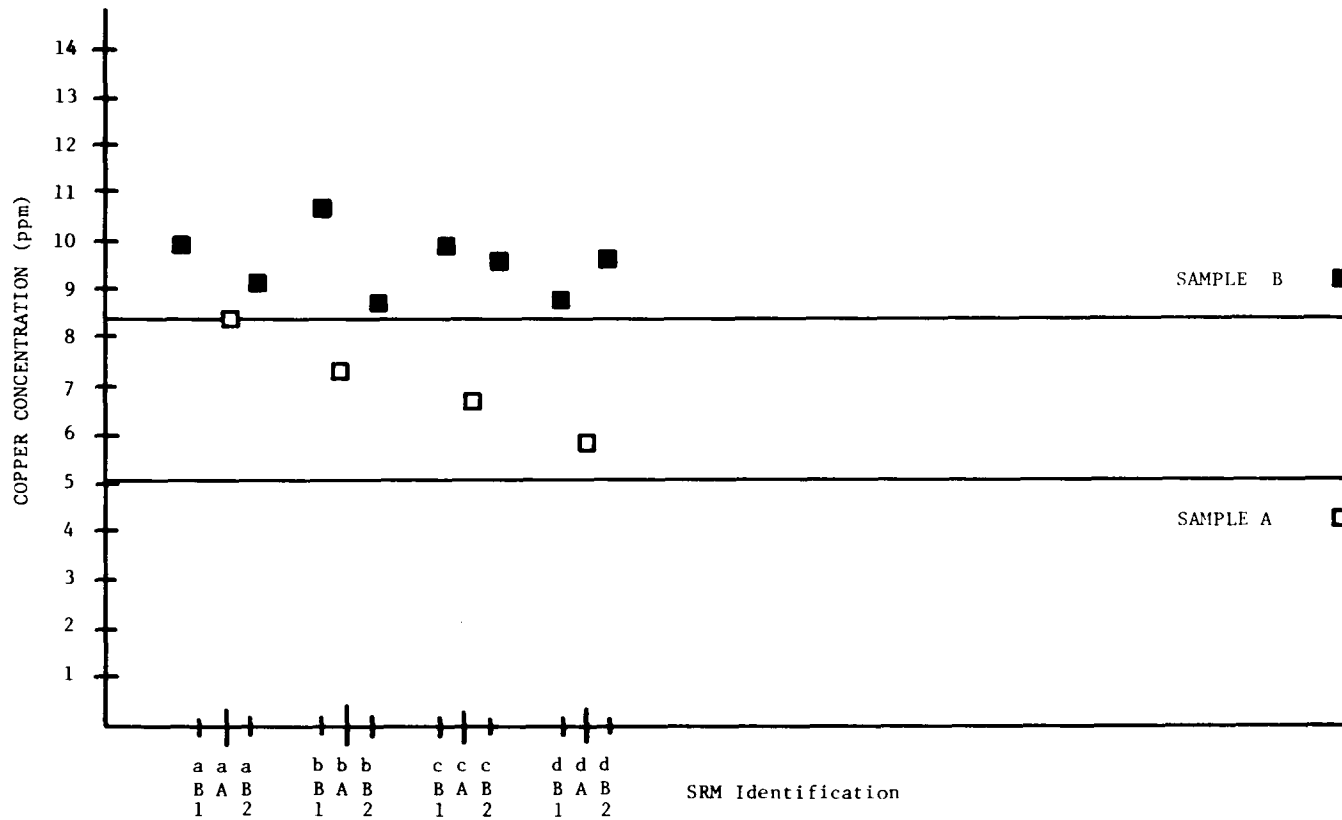
Figure 31. Copper Quality Control Chart. The SRM identification on the x-axis corresponds to that given in Table 19 for unspiked sediments; the solid horizontal lines represent the median copper concentration in Sample A and Sample B obtained from the data on the underlay (Figure 6).
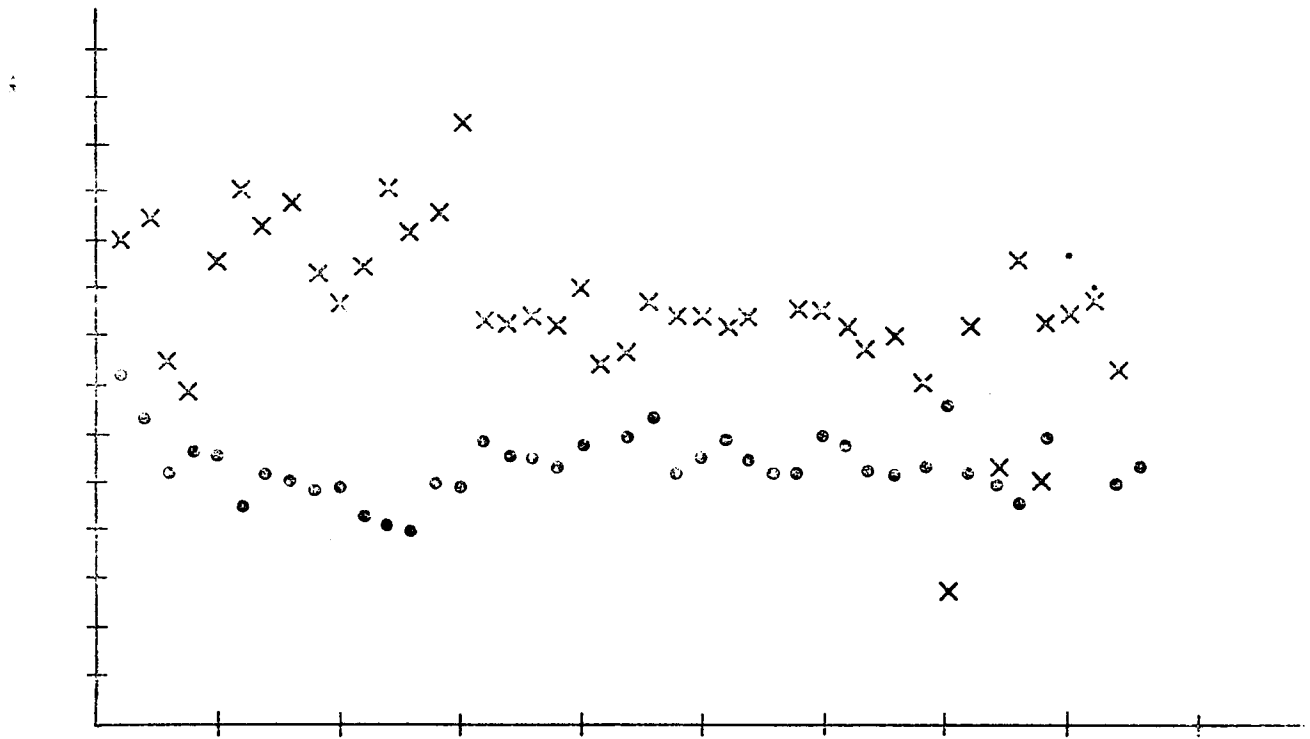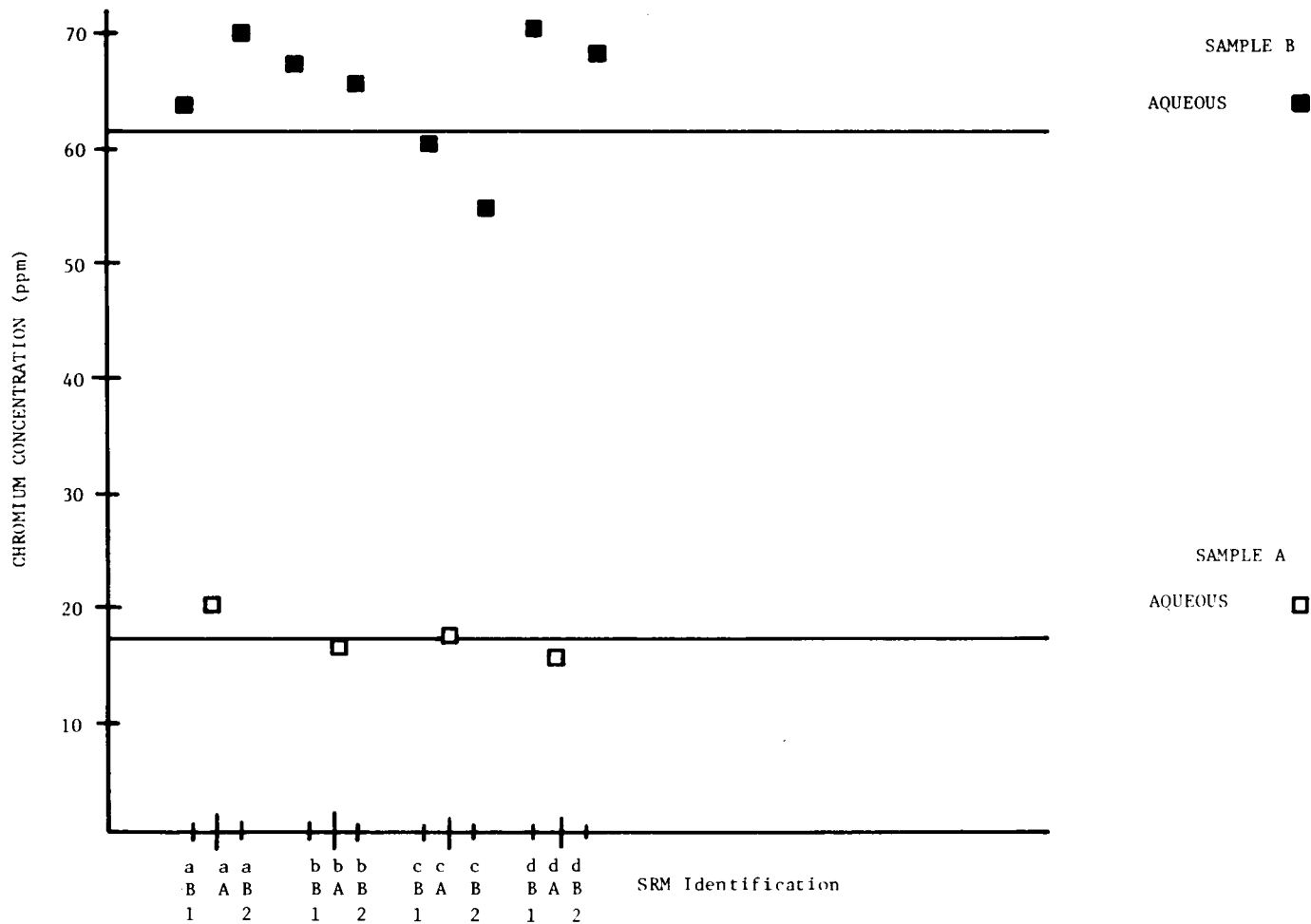
Figure 32. Chromium Quality Control Chart. The SRM identification on the x-axis corresponds to that given in Table 19 for unspiked sediments; the solid horizontal lines represent the median chromium concentration in Sample A and Sample B obtained from the data on the underlay (Figure 7).
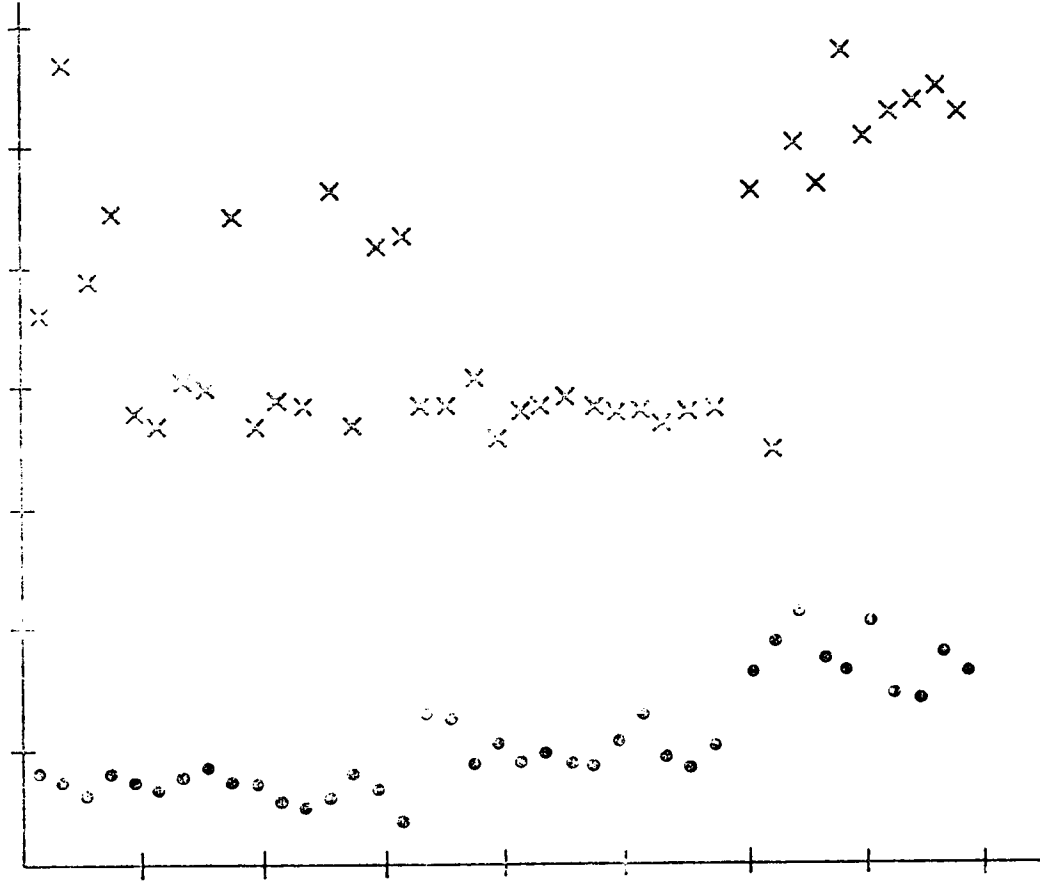
AAS analysis (Figure 26). The percent recovery of spikes,
however, was used as described below.

b. Vanadium

The SRM analysis for vanadium indicates that the diges-
tion process was in-control for all four sets of SRM-BLM
Sediments (Figure 27). Sample A-a was somewhat higher than
A-b, A-c, and A-d but Sample B analysis was consistent
throughout. A difference in vanadium content was observed
for aqueous versus matrix-matched standard calibration. The
matrix-matched value agreed well with Sample B content while
Sample A is more in line with aqueous calibration.

c. Cadmium

The SRM analysis for cadmium is similar to that for
barium (Figure 28). Due to the loss of cadmium during
flameless AAS analysis the values obtained fell below the
median value previously obtained for Sample A and Sample B.
Flame AAS analysis of set b and set d for Sample B performed
prior to the flameless AAS determination showed the SRM
digestion to be in-control. Cadmium was not detected in
Sample A for set b and d by flame AAS.

d. Lead

The lead content measured in the SRM samples was within
the range determined for the previous replicate analyses
indicating that the process was in-control for all four
digestion groupings (Figure 29).

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e.  Nickel

The median value for replicate nickel analysis of Sample
A and Sample B has not been firmly established.  Replicates
25-45 for Sample B were below the minimum detection limit
with nitrous oxide-acetylene operation.  Sample A replicate
analyses were performed with various flame systems and there-
fore should not be averaged.  The range of nickel concentra-
tion for the SRM's is consistent for the four sets of samples.
The nitrous oxide-acetylene flame system was employed to
minimize interference conditions.  In addition, a further
correction was contributed by measuring sample absorbance at
a nonabsorbing wavelength.  The consistency demonstrated with
SRM analysis suggests that the procedure is in-control
(Figure 30).

f.  Copper

The SRM copper analysis for Sample A was inconsistent,
especially for set a (Figure 31).  However, Sample B SRM
analysis was satisfactory and sufficiently reproducible to
warrant considering the analysis in-control.

g.  Chromium

The medium values represented by the lines on Figure 32
are those for replicate analyses 30-39.  Prior to replicate
30 the samples were analyzed by air-acetylene.  The hotter
nitrous oxide-acetylene flame was used for replicates 30-39
and subsequently for MAFLA sediments and SRM's.  The SRM

analysis for chromium indicates that the analysis was in-control.

h.  Iron

The iron analysis was not tested for in-control versus out-of-control since iron is not a trace metal component of sediments.  A judgment based on the analysis of a major component could lead to false conclusions since 20% to 30% errors could occur without a gross difference in iron content observed.

2.  <u>Percent Recovery of Spikes and Matrix Interference Applications</u>.  The amount of each trace element measured in both spiked and unspiked SRM's is given in Table 20 for aqueous calibration and in Table 21 for matrix-matched standards. Each value obtained for SRM analyses shown in Tables 20 and 21 was not plotted on the overlays in order to avoid confusion.  The percent recovery calculated from the data on Tables 20 and 21 is presented in Table 22 so that comparison may be easily made.  The discussion below will address accuracy, precision, and matrix interferences as determined by percent recovery of spikes since these areas are more conveniently treated as a group rather than individually.

a.  Barium

The losses or retarded atomization incurred for graphite furnace flameless analysis were based on the 50.8% recovery of the 50 ppm barium addition.  SRM set b was excluded for

| SRM | ppm Ba* | ppm V | ppm Cd* | ppm Pb | ppm Ni | ppm Cu | ppm Cr |
|---|---|---|---|---|---|---|---|
| A-a | 57.7 | 46.2 | 0.03 | 28.0 | 6.8 | 8.1 | 20.0 |
| A-sp-a | 84.7 | 126.0 | 15.7 | 77.4 | 66.9 | 57.0 | 76.3 |
| B-1-a | 8.7 | 10.8 | 0.20 | 8.5 | 1.3 | 10.0 | 63.5 |
| B-2-a | 7.9 | 10.2 | 0.21 | 7.9 | 1.4 | 9.0 | 70.0 |
| B-1-sp-a | 35.6 | 89.1 | 18.6 | 59.2 | 58.1 | 55.7 | 122.0 |
| B-2-sp-a | 36.1 | 87.5 | 18.3 | 56.4 | 60.1 | 54.1 | 121.0 |
| | | | | | | | |
| A-b | 47.1 | 32.8 | 0.03 | 28.8 | 7.0 | 7.4 | 16.4 |
| A-sp-b | 51.2 | 99.8 | 14.1 | 80.3 | 67.3 | 55.1 | 75.9 |
| B-1-b | 8.2 | 9.9 | 0.18 | 9.2 | 2.7 | 11.0 | 67.2 |
| B-2-b | 7.7 | 8.9 | 0.20 | 7.5 | 2.3 | 8.9 | 66.1 |
| B-1-sp-b | 11.1 | 74.9 | 25.7 | 55.5 | 59.3 | 59.1 | 125.4 |
| B-2-sp-b | 11.8 | 81.6 | 24.0 | 59.0 | 61.2 | 59.1 | 124.4 |
| | | | | | | | |
| A-c | 60.3 | 30.4 | 0.03 | 24.9 | 8.1 | 6.6 | 17.8 |
| A-sp-c | 70.2 | 96.2 | 16.2 | 72.7 | 57.2 | 54.2 | 76.0 |
| B-1-c | 7.3 | 10.3 | 0.20 | 7.6 | 2.1 | 9.9 | 59.6 |
| B-2-c | 7.0 | 7.9 | 0.25 | 7.1 | 1.4 | 9.6 | 52.4 |
| B-1-sp-c | 35.9 | 71.7 | 22.5 | 56.3 | 53.7 | 59.0 | 117.1 |
| B-2-sp-c | 38.6 | 74.8 | 20.3 | 50.8 | 52.7 | 58.4 | 113.3 |
| | | | | | | | |
| A-d | 55.0 | 35.5 | <D.L. | 21.6 | 7.3 | 5.8 | 14.9 |
| A-sp-d | 81.1 | 95.4 | 14.7 | 71.0 | 56.5 | 54.9 | 72.6 |
| B-1-d | 7.5 | 10.7 | 0.25 | 6.6 | 2.3 | 8.9 | 69.8 |
| B-2-d | 7.5 | 10.6 | 0.21 | 8.2 | 2.9 | 9.7 | 67.9 |
| B-1-sp-d | 32.0 | 77.4 | 22.1 | 51.5 | 58.8 | 56.5 | 126.9 |
| B-2-sp-d | 33.5 | 78.5 | 21.8 | 53.2 | 58.6 | 56.0 | 123.7 |
| Amount of Spike | 50 | 50 | 25 | 50 | 50 | 50 | 50 |

*Analyzed by Flameless AAS

Table 20. Analysis of SRM A and B for Ba, V, Cd, Pb, Ni, Cu, Cr using Aqueous Calibration Standards. Only aqueous standards were used for those elements that experience no matrix interference (Fe and Pb) and for those that were determined by flameless AAS (Cd and Ba).

| SRM | ppm V | ppm Ni | ppm Cu | ppm Cr |
|---|---|---|---|---|
| A-a | 38.4 | 7.7 | 9.4 | 17.4 |
| A-sp-a | 104.1 | 75.8 | 66.1 | 66.4 |
| B-1-a | 9.2 | 1.5 | 11.6 | 55.3 |
| B-2-a | 8.8 | 1.6 | 10.4 | 60.9 |
| B-1-sp-a | 73.8 | 65.8 | 64.6 | 106.1 |
| B-2-sp-a | 72.4 | 68.1 | 62.7 | 105.3 |
| | | | | |
| A-b | 27.4 | 8.0 | 8.6 | 14.3 |
| A-sp-b | 82.6 | 76.4 | 63.9 | 66.0 |
| B-1-b | 8.5 | 3.0 | 12.8 | 58.5 |
| B-2-b | 7.6 | 2.6 | 10.3 | 57.5 |
| B-1-sp-b | 62.0 | 67.3 | 68.6 | 109.1 |
| B-2-sp-b | 67.6 | 69.5 | 68.6 | 108.2 |
| | | | | |
| A-c | 25.5 | 9.2 | 7.7 | 15.5 |
| A-sp-c | 79.6 | 70.8 | 62.9 | 66.1 |
| B-1-c | 8.8 | 2.2 | 11.5 | 52.2 |
| B-2-c | 6.9 | 1.5 | 11.1 | 46.2 |
| B-1-sp-c | 59.5 | 60.9 | 68.5 | 101.9 |
| B-2-sp-c | 62.0 | 59.8 | 67.8 | 98.6 |
| | | | | |
| A-d | 29.6 | 8.3 | 6.7 | 12.9 |
| A-sp-d | 79.0 | 64.1 | 63.7 | 63.2 |
| B-1-d | 9.4 | 2.6 | 10.3 | 60.8 |
| B-2-d | 9.1 | 3.3 | 11.2 | 59.1 |
| B-1-sp-d | 64.1 | 55.4 | 67.9 | 110.4 |
| B-2-sp-d | 65.0 | 55.2 | 67.7 | 107.6 |

Table 21. Analysis of SRM A and B for V, Ni, Cu, and Cr using Matrix-
Matched Calibration Standards. Only aqueous standards
were used for those elements that experience no matrix
interference (Fe and Pb) and for those that were deter-
mined by flameless AAS (Cd and Ba).

| SRM | Ba | V(Aq) | V(M) | Cd | Pb | Ni(Aq) | Ni(M) | Cu(Aq) | Cu(M) | Cr(Aq) | Cr(M) |
|-----|-----|-------|------|-----|-----|--------|-------|--------|-------|--------|-------|
| A-a | 54.0 | 159.6 | 131.4 | 62.7 | 98.8 | 120.2 | 136.2 | 97.8 | 113.4 | 112.6 | 98.0 |
| B-1-a | 53.8 | 156.6 | 129.2 | 73.6 | 101.4 | 113.6 | 128.6 | 91.4 | 106.0 | 117.0 | 101.6 |
| B-2-a | 56.4 | 154.6 | 127.2 | 72.4 | 97.0 | 117.4 | 133.0 | 90.2 | 104.6 | 102.0 | 88.8 |
| Ave-a | 54.7 | 156.9 | 129.3 | 69.6 | 99.1 | 117.1 | 132.6 | 93.1 | 108.0 | 110.5 | 96.1 |
| A-b | 8.2 | 134.0 | 110.4 | 56.3 | 103.0 | 120.6 | 136.8 | 95.4 | 110.6 | 119.0 | 103.4 |
| B-1-b | 5.8 | 130.0 | 107.0 | 102.1 | 92.6 | 113.2 | 128.6 | 96.2 | 111.6 | 116.4 | 101.2 |
| B-2-b | 8.2 | 145.4 | 120.0 | 95.2 | 103.0 | 117.8 | 133.8 | 100.4 | 116.6 | 116.6 | 101.4 |
| Ave-b | 7.4 | 136.5 | 112.5 | 84.5 | 99.5 | 117.2 | 133.1 | 97.3 | 112.9 | 117.3 | 102.0 |
| A-c | 19.8 | 131.6 | 108.2 | 24.7 | 95.6 | 98.2 | 123.2 | 95.2 | 110.4 | 116.4 | 101.2 |
| B-1-c | 57.2 | 122.8 | 101.4 | 89.2 | 97.4 | 103.2 | 117.4 | 98.2 | 114.0 | 115.0 | 99.4 |
| B-2-c | 63.2 | 133.8 | 110.2 | 80.2 | 87.4 | 102.6 | 116.6 | 97.6 | 113.4 | 121.8 | 104.8 |
| Ave-c | 46.7 | 129.4 | 106.6 | 64.7 | 93.6 | 101.3 | 119.1 | 97.0 | 112.6 | 117.7 | 101.8 |
| A-d | 52.2 | 119.8 | 98.8 | - | 98.8 | 98.4 | 127.6 | 98.2 | 114.0 | 115.4 | 100.6 |
| B-1-d | 49.0 | 133.4 | 109.4 | 87.4 | 89.8 | 113.0 | 115.2 | 95.2 | 110.4 | 114.2 | 99.2 |
| B-2-d | 52.0 | 135.8 | 111.8 | 86.4 | 90.0 | 111.4 | 113.0 | 92.6 | 107.6 | 111.6 | 97.0 |
| Ave-d | 51.1 | 129.7 | 106.7 | 86.9 | 92.9 | 107.6 | 118.6 | 95.3 | 110.7 | 113.7 | 98.9 |
| Ave: a,b,c,d | 50.8 | 138.1 | 113.8 | 76.4 | 96.2 | 110.8 | 125.8 | 95.7 | 111.0 | 114.8 | 99.7 |

Table 22. Percent Recovery of Spikes for SRM's Calculated from Data in Table 20 and Table 21; Aq=Aqueous; M=Matrix-Matched. The spiked samples contained 50 ppm of added Ba, V, Ni, Cu, Cr and 25 ppm of added Cd.

this computation since the barium spikes were obviously not added correctly. The 19.8% recovery for A-c and 63.2% for B-2-c are suspect but were included in the average. Since multiple pipetting was required, it is conceivable that these two samples were confused by omitting part of the spikes for A-c and adding this portion to B-2-c instead. Sets a and d agree quite well and add credence to the assumption made above. The barium values measured for the MAFLA sediments were increased to account for the loss of barium indicated in Table 22. The retention of barium in the complex matrix is a more probable explanation for low recovery than volatility considerations.

b. Vanadium

The recovery of vanadium spikes was consistently high both for aqueous (138.1%) and matrix-matched (113.8%) standard calibration. The matrix-matched standards provided a 25% correction but recoveries remained high by 14%. The vanadium measured in set a was greater than for sets b, c, and d by 10 ppm. Precision was good when measurements for sets b, c, and d were compared.

The improvement in recovery with matrix-matched standard calibration indicated a matrix interference. The fact that values were 100% was due to the enhancement effect of matrix interferents on vanadium absorbance previously reported (1).

However, the 113.8% recovery was not acceptable since the interference was not completely eliminated.

The vanadium analysis of SRM Set a was repeated in addition to the MAFLA Sediments in order to investigate the high percent recovery and the high values measured for Set a. This analysis included measurement of absorbance at a nonabsorbing vanadium wavelength and for the analytical vanadium wavelength. The concentration of vanadium and percent recovery of vanadium spikes were calculated for three cases:

1.  Analytical wavelength absorbance for aqueous standard calibration;

2.  Analytical wavelength absorbance for matrix-matched standard calibration; and

3.  Analytical wavelength absorbance minus nonabsorbing wavelength absorbance for matrix-matched standard calibration.

The data obtained by the three treatments is presented in Table 23. The concentration of vanadium obtained is in line with Sets b, c and d for the repeat analysis. The non-absorbing wavelength correction was needed to properly compensate for interferences present resulting in ∿100% recovery of spikes. The nonabsorbing correction for each of the MAFLA Sediments was used to calculate the refined vanadium data (Appendix B).

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| SRM | V Concaentration (ppm) | | | Percent Recovery | | |
|-----|------|------|------|-------|-------|------|
| SRM | 1* | 2† | 3 # | 1* | 2† | 3 # |
| A-a | 33.4 | 28.0 | 26.8 | 127.6 | | |
| A-sp-a | 97.2 | 81.5 | 76.2 | 127.6 | 107.0 | 98.8 |
| B-1-a | 10.6 | 8.9 | 9.3 | | | |
| B-2-a | 10.4 | 8.7 | 9.1 | | | |
| B-1-sp-a | 75.6 | 63.4 | 60.1 | 130.4 | 109.0 | 101.6 |
| B-2-sp-a | 74.3 | 62.3 | 58.8 | 127.8 | 107.2 | 99.4 |
| | | | Average | 128.6 | 107.7 | 99.9 |

* 1. Analytical absorbing wavelength:  Aqueous

† 2. Analytical absorbing wavelength:  Matrix-Matched

# 3. Analytical minus nonabsorbing wavelength absorbance:
   Matrix-Matched.

Table 23.   Concentration of Vanadium and Percent Recovery of
Spikes for SRM Set a by Three Methods.

c. Cadmium

The precision of the SRM cadmium determinations was good. The minimum detection limit was exceeded for A-d. All 4 sets were included in the average percent recovery computation. Comparison of the recovery for sets c and d was better than for a and b groupings. The analyses for cadmium was not as precise as that for barium. Although both were analyzed by the same method, cadmium is the more volatile of the two which can account for variation in losses. The measured cadmium values for the MAFLA sediments were adjusted upward to compensate for the losses in drying and charring steps for flameless operation.

d. Lead

The average recovery of lead spikes was 96.2% by calibration with aqueous standards. The data obtained for the four SRM sets demonstrates good precision. The recovery values obtained negates the consideration of matrix interferences for accurate lead determinations.

e. Nickel

The SRM nickel analyses generated data of acceptable precision. The percent recovery of nickel spikes averaged 110.8% and 125.8% for aqueous and matrix-matched calibration respectively. The high recovery is similar to that for vanadium but is higher for matrix-matched as opposed to aqueous standard comparisons.

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SRM Sets a and c were reanalyzed with the MAFLA Sediments employing the nonabsorbing wavelength correction for nickel. The data obtained for set a and c is presented in Table 24 calculated as follows:

1. Analytical wavelength absorbance for aqueous standard calibration;

2. Analytical wavelength absorbance for matrix-matched standard calibration; and

3. Analytical wavelength absorbance minus nonabsorbing wavelength absorbance for matrix-matched standard calibration.

The unspiked SRM nickel values as compared to matrix-matched standards following nonabsorbing wavelength correction was identical to the uncorrected values obtained with aqueous standards. The spiked SRM's exhibited a significant absorbance at the nonabsorbing wavelength yielding 15% lower nickel concentrations. The resultant percent recovery was excellent (average of 100.5). Therefore, the data presented in Appendix B for nickel content in the MAFLA Sediments was obtained by subtracting the nonabsorbing wavelength signal from the analytical wavelength absorbance. A matrix interference was evident however, since the matrix-matched standards were required for quantitative recovery.

| | Ni Concentration (ppm) | | | Percent Recovery | | |
|---|---|---|---|---|---|---|
| SRM | 1* | 2† | 3# | 1* | 2† | 3# |
| A-a | 7.7 | 8.7 | 7.7 | | | |
| A-sp-a | 67.3 | 76.2 | 58.1 | 119.2 | 135.0 | 100.8 |
| B-1-a | 2.5 | 2.8 | 2.5 | | | |
| B-2-a | 2.3 | 2.6 | 2.3 | | | |
| B-1-sp-a | 59.2 | 67.1 | 54.2 | 113.4 | 128.6 | 103.4 |
| B-2-sp-a | 60.8 | 68.8 | 54.0 | 117.0 | 132.4 | 103.4 |
| | | | | | | |
| A-c | 8.0 | 9.0 | 8.0 | | | |
| A-sp-c | 62.7 | 71.0 | 57.6 | 109.4 | 123.4 | 99.2 |
| B-1-c | 2.2 | 2.5 | 2.2 | | | |
| B-2-c | 2.0 | 2.3 | 2.0 | | | |
| B-1-sp-c | 54.0 | 61.2 | 51.4 | 103.6 | 117.4 | 98.4 |
| B-2-sp-c | 53.7 | 60.8 | 50.9 | 103.4 | 117.0 | 97.8 |
| | | | Average: | 111.0 | 125.6 | 100.5 |

* 1. Analytical absorbing wavelength:  Aqueous

† 2. Analytical absorbing wavelength:  Matrix-matched

# 3. Analytical minus nonabsorbing wavelength absorbance:
  Matrix-matched

Table 24. Nickel Concentrations and Percent Recovery of Spikes for SRM Set a. The data is calculated on the basis of three different methods.

f. Copper

The analysis of the four sets of SRM's for copper pro-
duced data of comparable values indicating good precision.
The percent recovery obtained by aqueous standard calibration
was somewhat low (95.7) while high recoveries resulted from
matrix-matched standard calculations (111.0). The samples
produced no background absorbance similar to that observed
for vanadium and nickel. The aqueous standard calculations
more closely approximated quantitative recovery of spikes.
Apparently the matrix-matched standards were not required
for correction of matrix interferences or were not represen-
tative of these interferences. The MAFLA Sediments contained
20% calcium while the SRM's contained only trace amounts.
Therefore it is not possible to determine from the SRM
copper analysis if the matrix correction should be applied
to the MAFLA Sediment analyses.

Allen reported an interference from 1% sodium, potassium,
and calcium for copper determinations using a dc photometric
system (32). This interference was not found for ac photo-
metric operation. The modern AAS instruments, such as those
at GSRI, are ac photometric systems which discriminate
against interferences from flame emission. This interference
was present for flame AAS analysis for barium. It is
reasonable to assume that flame emission noise from calcium

could interfere with copper measurements. Although no experiments have been performed at GSRI to confirm this theory, we feel that the matrix-matched standard calibration produces more accurate data than that obtained by ignoring the complex matrix.

g. Chromium

The reproducability of SRM chromium analysis was somewhat better for Sample B than Sample A. The values were within the proper range established by previous replicate analysis (Figure 32).

The recovery of chromium spikes was 114.8% for aqueous standard comparison and 99.7% for matrix-matched standard calibration. The presence of the matrix interference on chromium analyses is further confirmed by these recoveries. The quantitative recovery obtained by matrix-matched calibrations illustrates the need for this correction. As expected, no signal was observed by monitoring absorbance at a nonabsorbing chromium wavelength.

B. Statistical Analysis of MAFLA Sediment Data

The sediment data was compared by calculating the average concentration, standard deviation and relative standard deviation for each metal for duplicate sets a and b (Table 25). The statistical analysis illustrates that duplicate analyses were performed with good reproducibility.

| Element | Calibration Standard | Average Concentration (ppm) | | | Standard Deviation (ppm) | | | Relative Standard Deviation (ppm) | | | Samples Excluded: |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Set a | Set b | Set a + b | Set a | Set b | Set a + b | Set a | Set b | Set a + b | Obvious "Spikes" |
| Ba | Aqueous | 23.7 | 21.7 | 22.7 | 12.1 | 10.0 | 11.2 | 51.1 | 46.1 | 49.3 | |
| V | Aqueous | 11.6 | 11.1 | 11.4 | 8.5 | 8.2 | 8.3 | 73.3 | 73.9 | 72.8 | 54-31 |
| | Matrix | 9.6 | 9.2 | 9.4 | 7.0 | 6.7 | 6.9 | 72.9 | 72.8 | 73.4 | 54-31 |
| Cd | Aqueous | 0.082 | 0.09 | 0.086 | 0.039 | 0.055 | 0.047 | 47.6 | 61.1 | 54.7 | |
| Pb | Aqueous = Matrix | 5.0 | 4.4 | 4.7 | 1.8 | 2.1 | 1.9 | 36.0 | 47.7 | 40.4 | |
| Ni | Aqueous | 5.9 | 6.4 | 6.1 | 3.4 | 4.0 | 3.7 | 57.6 | 62.5 | 60.7 | 2-2 |
| | Matrix | 6.6 | 7.2 | 6.9 | 3.9 | 4.5 | 4.2 | 59.1 | 62.5 | 60.9 | 2-2 |
| Cu | Aqueous | 1.9 | 1.8 | 1.8 | 1.7 | 1.9 | 1.8 | 89.5 | 105.6 | 100.0 | 54-31 |
| | Matrix | 2.2 | 2.1 | 2.1 | 2.0 | 2.1 | 2.0 | 82.7 | 100.0 | 95.2 | 54-31 |
| Cr | Aqueous | 16.4 | 14.5 | 15.4 | 6.9 | 8.7 | 7.8 | 42.1 | 60.0 | 50.6 | |
| | Matrix | 14.4 | 12.9 | 13.6 | 6.0 | 7.8 | 6.9 | 41.7 | 60.5 | 50.7 | |
| Fe | Aqueous = Matrix | 5017 | 4737 | 4877 | 4651 | 4578 | 4614.5 | 92.7 | 96.6 | 94.6 | |

Table 25. Statistical Analysis of Sediment Data, MAFLA II.
Only aqueous standards were used for those elements
analyzed by flameless techniques (Ba and Cd).

The averages for set a and set b were more variable for nickel and chromium determinations than for the other elements.  For nickel poor duplicates were obtained for samples 16, 22, 26, 27, 54 and 63. Four duplicates differed significantly for chromium analysis: samples 3, 7, 11, and 26.  The acid extracts for these sample pairs were reanalyzed for nickel and chromium.  The poor duplicates were reproduced in each case.

Experiments performed at GSRI varying the sediment digestion parameters for time and temperature produced curves that provide an explanation for poor duplicate analyses (33).  The graphs of concentration (ppm) versus digestion time for three temperatures ($35^{\circ}$C, $65^{\circ}$C, $95^{\circ}$C) are shown in Figure 33 and Figure 34 for nickel and chromium, respectively.  It is apparent from these diagrams that small temperature variations result in extraction of different amounts of metal.  The EPA recommended digestion time of 15 minutes is located on the rising portion of both curves; measurements taken during this interval will exhibit significantly more variation than those on the plateau of the curve.  The time and temperature variation can, therefore, contribute to errors in both accuracy and precision.  The digestion pattern shown for nickel and chromium varies depending upon the specific element for the other elements of interest here.  Cadmium, barium, and lead curves plateau at 15 min. for all three temperatures (Figures 35, 36, and 37); accuracy and precision should be improved for these metals as shown in Table 25. Vanadium and iron analyses were similar in that plateaus were

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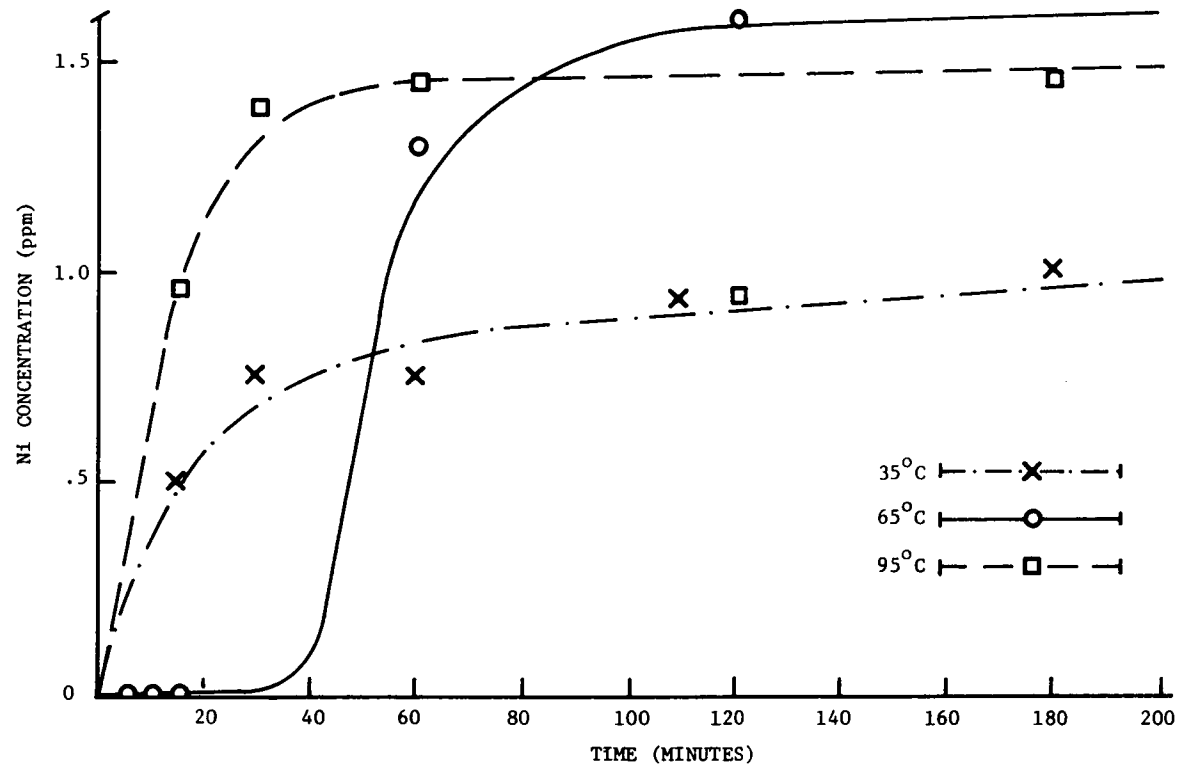
Figure 33. Results of Kinetics Experiment for Nickel. Note that the limiting value at 35°C is approximately half of that at 65° and 95°.
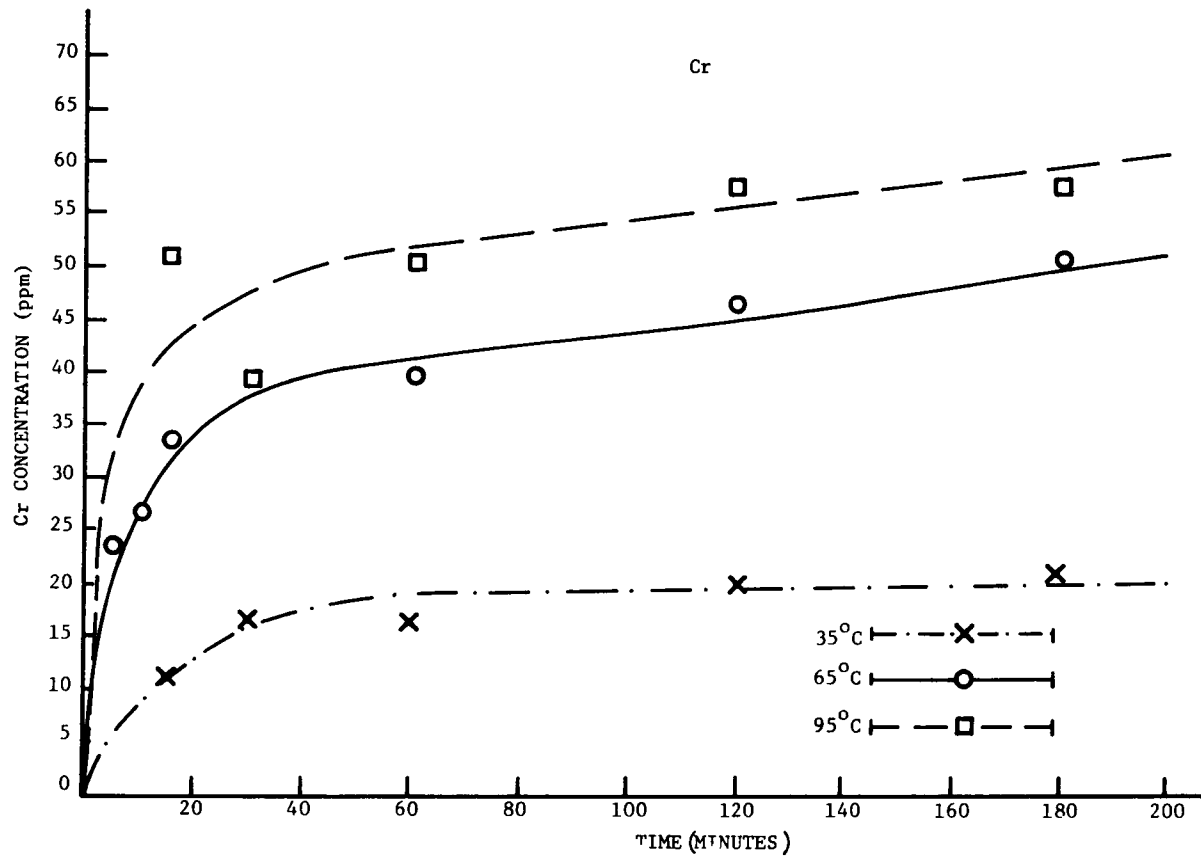
Figure 34.   Results of Kinetics Experiment for Chromium.   This graph illustrates the effects of varying digestion
temperatures and times on the recovery of Chromium from SRM sediment B.
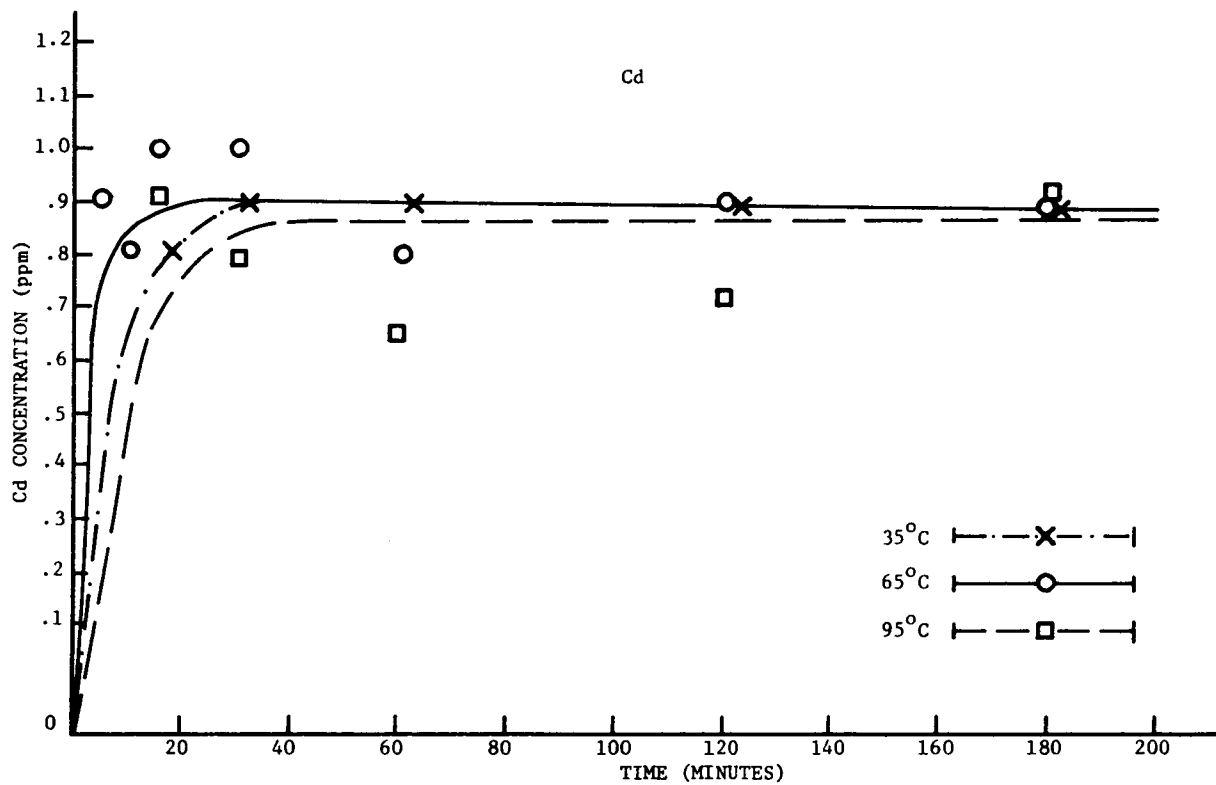
Figure 35. Results of Kinetics Experiment for Cadmium. This graph illustrates the effect of varying digestion temperature and time on the recovery of cadmium from SRM sediment B.
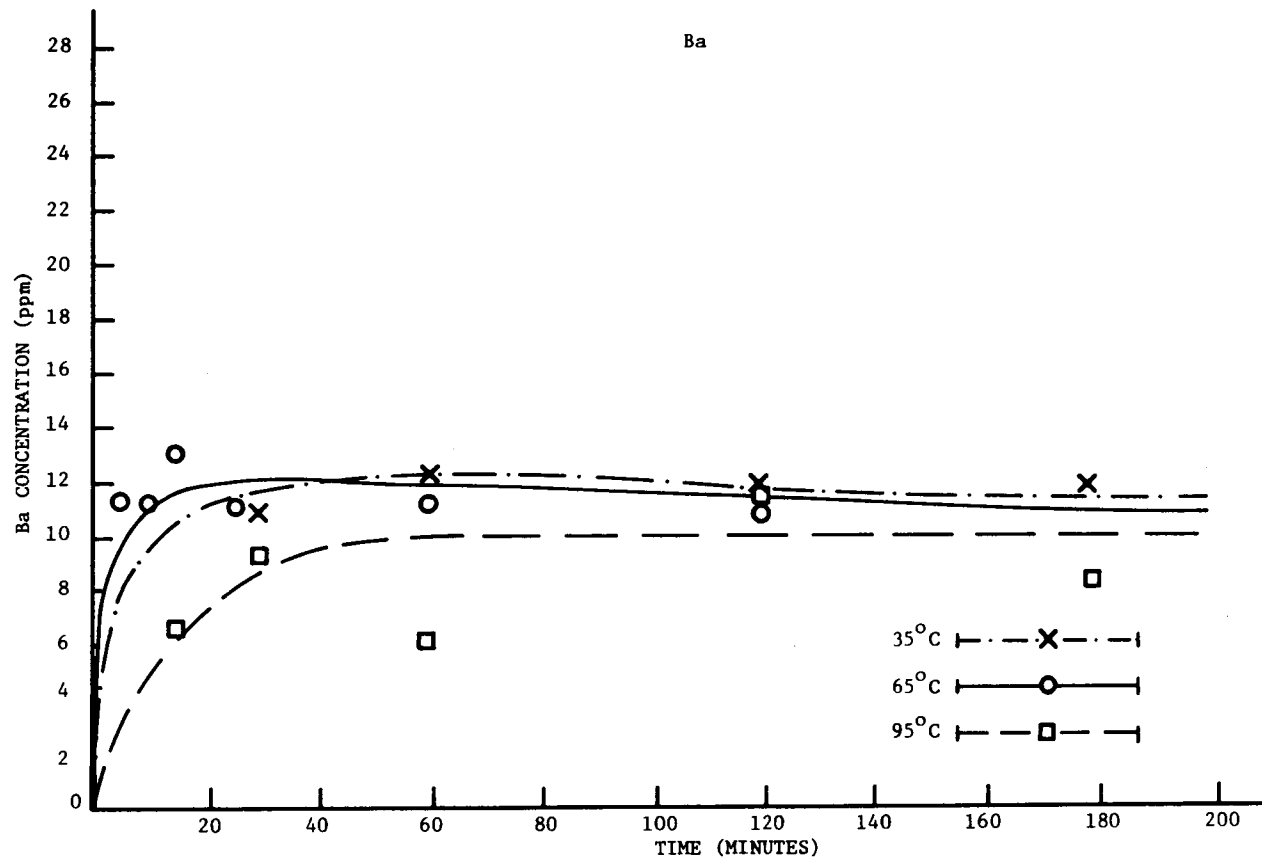
Figure 36. Results of Kinetics Experiment for Barium. Note that most of the barium is extracted from the sediments at 65° and 95° within a few minutes.
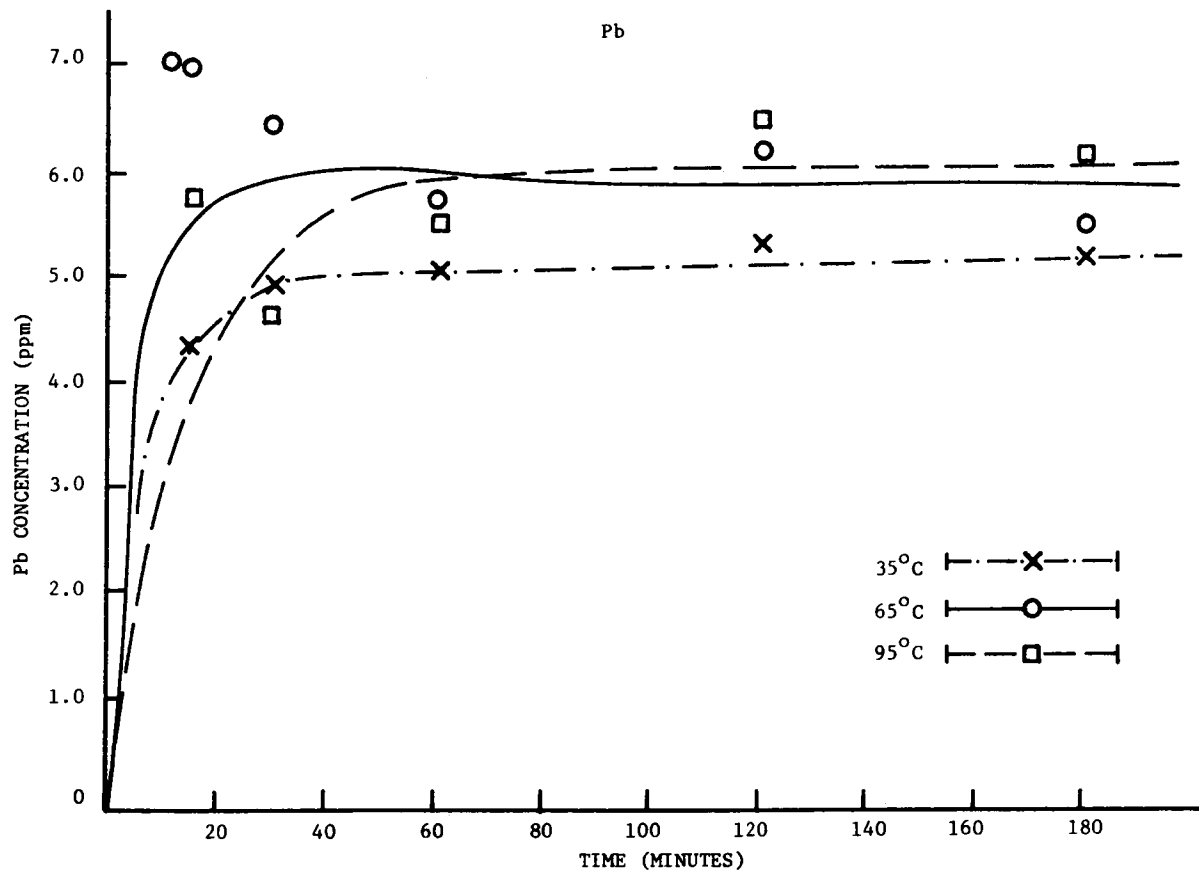
Figure 37. Results of Kinetics Experiment for Lead. The lead concentration reaches its limiting value within a relatively short time.

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obtained early at $30^{\circ}C$ and $65^{\circ}C$. No plateau was reached at $95^{\circ}C$ after 3 hours (Figures 38 and 39). The need for exhaustive standardization of digestion methodology was demonstrated by this series of experiments. The digestion time is currently under investigation by the Environmental Protection Agency, Region IV Office, Athens, Georgia.

The standard deviation and relative standard deviation shows the variability of trace metal levels within the groups of 35 sediments. Good precision is demonstrated for comparisons of set a, set b and set (a + b) data.

Further analysis of the level of reproducibility is given in Table 26 which contains the relative standard deviation for duplicates as compared to the value obtained for set a in each case. Interpretation of this table is complicated by the fact that differences appear greater for metals present in very low concentrations. For example, iron agreement is excellent while cadmium deviations are greatest. This chart is presented primarily for the convenience of selecting those samples demonstrating drastic differences in duplicate analyses.

The overall average variability for the 12 columns is 27.89%, including the minimum Fe and maximum Cd figures yields an overall average of 23.92%. The evaluation of the relative degree of reproducibility for duplicate demonstrations and duplicate instrumental analyses were performed on different days in all cases.
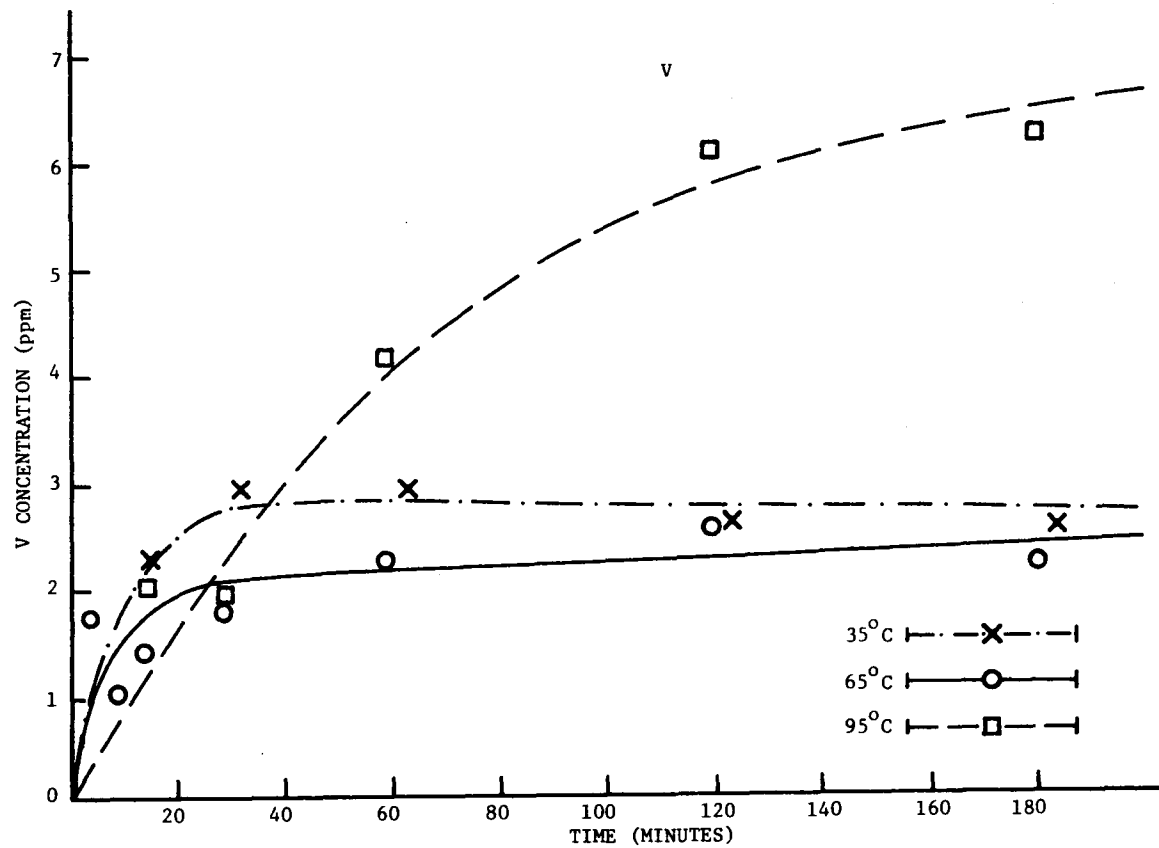
Figure 38. Results of Kinetics Experiment for Vanadium. This illustration shows that the amount of vanadium extracted varies radically with temperature and does not plateau after 3 hours for 95°C extraction.
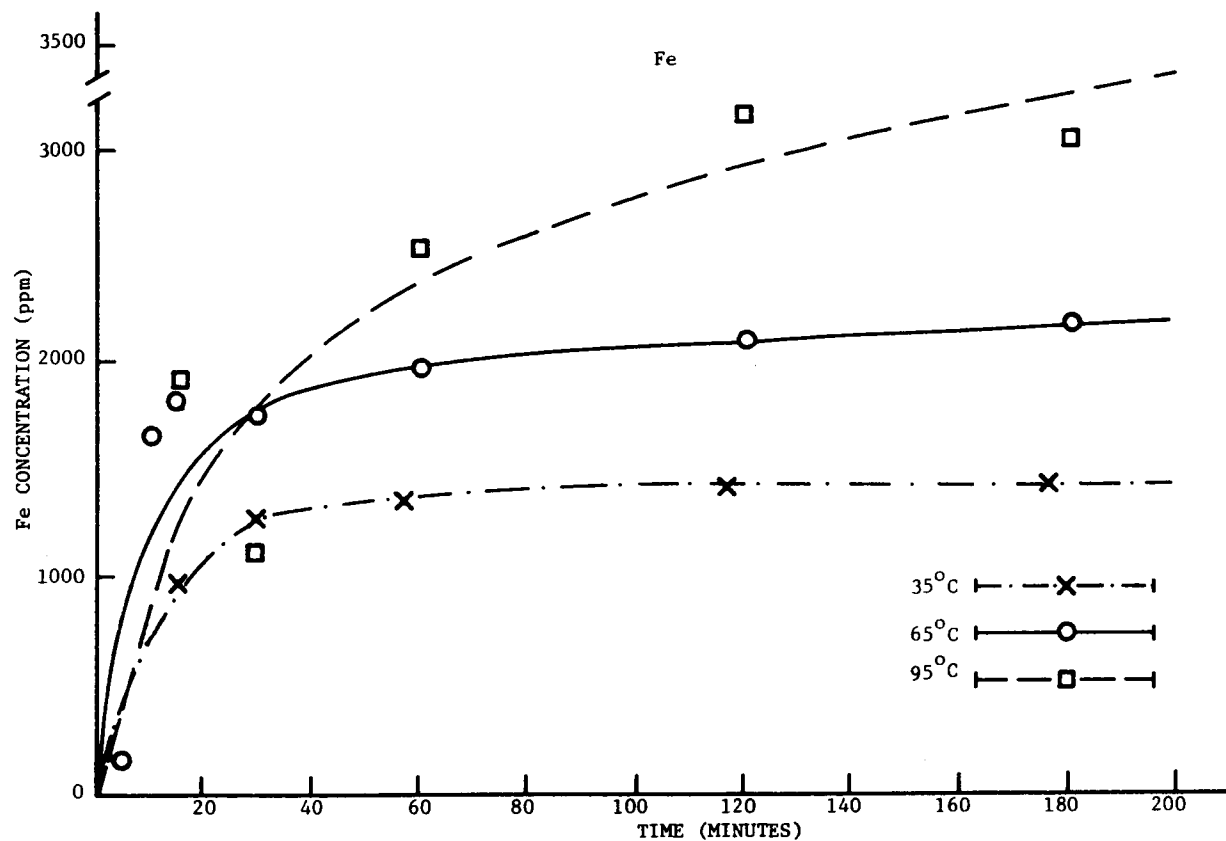
Figure 39.  Results of Kinetics Experiment for Iron.  This illustration shows that the amount of iron extracted varies radically with temperature and does not plateau after 3 hours for 95°C.

Percent Deviation

| BLM SAMPLE I.D. | GSRI SAMPLE I.D. | Ba | V Aqueous | V Matrix | Cd | Pb | Ni Aqueous | Ni Matrix | Cu Aq. | Cu Matrix | Cr Aqueous | Cr Matrix | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1-1 | 20.2 | 7.6 | 6.0 | - | - | 7.4 | 11.9 | 48.0 | 48.3 | 4.03 | 4.5 | 18.7 |
| 2 | 2-2 | - | - | - | 71.4 | 40.0 | 4.1 | - | - | - | 17.5 | 17.9 | 0.4 |
| 3 | 3-3 | 62.6 | 17.8 | 17.4 | 220.0 | - | 4.9 | 4.5 | 24.1 | 26.5 | 77.9 | 78.3 | 8.3 |
| 5 | 5-4 | 32.5 | 32.1 | 32.0 | 47.4 | 40.6 | 35.0 | 42.2 | 33.3 | 40.0 | 8.84 | 8.9 | 19.7 |
| 6 | 6-5 | 25.6 | 12.8 | 12.5 | 40.0 | 59.3 | 18.2 | 25.9 | 58.3 | 60.0 | 0.8 | 0.9 | 22.3 |
| 7 | 7-6 | 9.1 | - | - | 75.0 | - | 12.5 | 11.4 | - | - | 30.9 | 31.1 | 10.9 |
| 9 | 9-7 | 5.53 | 56.3 | 56.9 | 41.7 | - | 130.0 | 142.9 | - | - | 23.8 | 23.8 | 45.5 |
| 11 | 11-8 | 27.97 | 23.5 | 28.6 | 75.0 | 5.3 | 12.8 | 14.3 | 6.7 | 8.3 | 77.6 | 77.9 | 0.8 |
| 13 | 13-9 | 2.68 | 59.0 | 58.5 | - | 7.0 | 17.2 | 15.7 | 20.0 | 17.4 | 10.9 | 11.5 | 5.0 |
| 16 | 16-10 | 4.55 | 21.7 | 22.4 | 33.3 | 40.0 | 31.0 | 27.7 | 60.0 | 33.3 | 1.0 | 1.1 | 23.3 |
| 19 | 19-11 | 22.35 | 23.9 | 23.7 | 33.3 | 37.5 | 3.7 | 5.0 | - | 14.3 | 2.9 | 3.2 | 10.2 |
| 22 | 22-12 | 26.27 | 14.7 | 14.3 | 28.6 | 41.7 | 55.1 | 62.3 | 18.5 | 24.2 | 7.1 | 7.3 | 13.0 |
| 24 | 24-13 | - | - | - | 30.0 | 16.0 | - | - | - | - | 6.7 | 6.4 | 5.1 |
| 25 | 25-14 | 53.12 | 26.6 | 27.5 | - | 37.7 | 41.0 | 38.1 | - | - | 6.9 | 4.5 | 8.2 |
| 26 | 26-15 | 118.45 | 17.9 | 17.6 | 28.6 | 41.0 | 40.6 | 38.5 | 4.7 | 6.1 | 73.6 | 89.1 | 7.4 |
| 27 | 27-16 | 21.41 | 9.6 | 10.2 | 6.3 | 24.7 | 18.4 | 8.9 | 23.1 | 12.5 | 7.1 | 7.3 | 23.1 |
| 28 | 28-17 | 28.89 | 27.1 | 27.1 | 66.6 | 37.1 | 28.4 | 28.9 | 75.0 | 66.7 | 18.8 | 18.6 | 6.8 |
| 29 | 29-18 | 3.61 | 5.7 | 6.0 | 33.3 | 1.8 | 2.2 | 2.0 | 31.8 | 34.6 | 13.7 | 13.9 | 1.4 |
| 30 | 30-19 | 1.85 | 135.0 | 145.0 | 40.0 | - | 16.7 | 10.0 | 60.0 | 33.3 | 14.3 | 15.0 | 17.0 |
| 32 | 32-20 | 13.57 | - | - | 14.3 | 18.4 | 31.6 | 31.1 | 46.5 | 38.5 | 22.7 | 23.1 | 5.6 |
| 33 | 33-21 | 31.96 | 16.9 | 17.2 | - | 5.88 | 34.0 | 33.3 | - | - | 18.0 | 18.3 | 1.8 |
| 34 | 34-22 | 34.78 | 12.7 | 12.7 | 14.3 | 3.63 | 16.9 | 16.8 | 32.1 | 35.3 | 11.1 | 11.3 | 0.1 |
| 36 | 36-23 | 3.13 | 15.6 | 1.9 | - | 1.01 | 13.0 | 14.8 | 33.3 | 50.0 | 17.1 | 16.7 | 5.7 |
| 38 | 38-24 | 2.13 | 40.0 | 15.3 | - | 35.6 | 5.9 | 10.0 | - | - | 12.9 | 11.5 | 9.1 |
| 39 | 39-25 | 17.45 | 43.8 | 45.2 | 66.6 | 8.89 | 12.1 | 19.0 | 10.0 | - | 7.4 | 7.2 | 11.6 |
| 41 | 41-26 | 12.63 | 11.4 | 11.0 | 150.0 | 32.9 | 1.6 | 1.4 | 8.0 | 6.9 | 18.6 | 18.4 | 1.2 |
| 42 | 42-27 | 21.43 | 46.0 | 40.5 | 62.5 | 16.7 | 55.2 | 52.9 | - | - | 15.7 | 15.3 | 4.0 |
| 44 | 44-28 | 7.07 | 9.7 | 10.2 | 150.0 | - | 40.3 | 40.9 | 13.9 | 15.4 | - | - | - |
| 48 | 48-29 | 19.51 | 10.3 | 10.4 | 55.5 | 9.1 | 18.4 | 19.8 | - | - | 12.1 | 12.1 | 20.5 |
| 49 | 49-30 | 37.17 | 2.9 | 2.8 | 33.3 | 68.8 | 23.7 | 23.6 | 13.0 | 19.2 | 7.7 | 7.8 | 4.0 |
| 54 | 54-31 | 8.33 | 4.2 | 4.1 | - | 10.5 | 42.1 | 42.0 | 3.8 | 3.8 | 8.0 | 8.0 | 5.9 |
| 56 | 56-32 | 51.96 | 13.5 | 5.1 | 200.0 | 57.1 | 12.0 | 20.4 | - | 33.3 | 12.4 | 11.4 | 3.8 |
| 57 | 57-33 | - | - | - | 37.5 | 18.8 | 13.4 | 15.4 | - | - | 6.7 | 6.2 | 0.2 |
| 60 | 60-34 | - | - | - | 44.4 | - | 1.1 | 17.9 | - | - | 13.4 | 13.6 | 6.3 |
| 63 | 63-35 | 43.89 | 26.0 | 24.6 | 14.3 | 47.8 | 294.0 | 300.0 | - | - | 17.8 | 18.0 | 9.6 |
| Average for Group | | 24.90 | 25.67 | 24.37 | 61.19 | 27.31 | 32.19 | 34.83 | 29.70 | 28.54 | 17.82 | 18.24 | 9.90 |

Table 26. Relative Standard Deviation in Trace Metal Content Between Duplicate Samples, a and b. The relative standard deviation is given as $\frac{|a - b|}{a} \times 100$.

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CHAPTER V


TRACE METAL ANALYSIS OF MAFLA SEAWATER SAMPLES


A. Sample Preparation

The analysis of seawater for barium, vanadium, cadmium, lead, nickel, copper, chromium, and iron was complicated by the inadequate volume of sample (400 ml) received. GSRI used the ammonium pyrrolidine dithiocarbamate - methyl isobutyl ketone (APDC-MIBK) extraction procedure recommended in the 1971 Environmental Protection Agency Manual to analyze for six metals in seawater samples under a previous government contract (34). This procedure was found to be inappropriate for several reasons:

1. The method was designed for fresh water analysis; seawater was specified as presenting "some problems."

2. The efficiency of one extraction rather than multiple extraction was not specified.

3. The stability of the metal-APDC complex was not specified when in fact it was quite unstable. GSRI determined that three hours was probably a liberal estimate of stability if the extracts were immersed in an ice-bath and kept at low temperature during analysis. It was often impossible to analyze for 6 metals during this limited time period.

4. The amount of sample was highly underestimated (50 - 100 ml) for multiple metal determinations.

5. Accuracy was extremely poor as determined by extraction of EPA Standard Reference samples (not seawater of course).

6. Precision was extremely poor as determined by duplicate analyses of standards and samples.

7. The volume of standard (in-house) solution recommended was insufficient; two sets of standards were required for 6 metals to be read by AAS.

8. Standard calibration curves demonstrated lack of linearity and irreproducibility from the first set to the second set (probably due more to instability of the metal complex than poor analytical treatment).

9. The procedure was extremely time-consuming; the extraction procedure requires 8 hours for 12 samples and standards; and AAS analysis for 6-8 metals involves an additional 4-5 hrs. It was necessary for GSRI to operate on a shift basis due to complex instability since the extracts were not stable (even if frozen) overnight.

10. As regards the BLM OCS study: barium is not extracted by this procedure necessitating extraction with 0.1 M Thenoyltrifluoroacetone in MIBK. The method referenced for barium analysis of the seawater samples for this study produced ambiguous results (35). In addition, it was not officially sanctioned by the Environmental Protection Agency.

The most recent EPA Manual, Methods for Chemical Analysis of Water and Wastes, 1974, has substituted a different procedure for the one in

the 1971 publication (36). The extraction is performed with pyrrolidine dithiocarbamic acid (PDCA) in chloroform. The APDC-MIBK is mentioned as an alternate method but difficulties are also described.

## B.  Dissolved Metals

Due to the problems cited above and the insufficient sample volume provided, alternatives were considered. The flameless graphite furnace AAS technique was tested for applicability to seawater analysis (37). Standards were prepared using synthetic seawater for which certified trace metal quantitative information was supplied by the manufacturer (Instant Ocean, Aquarium System, Inc.). Trace metals required for aquarium nutrient supply are added from a separate packet so that these could be eliminated from the standard solution prepared. The flameless ASS procedure is not ideal for seawater analysis due to the high salt content. It was possible to analyze for barium, vanadium, chromium, and iron by this technique. The programming of HGA Graphite Furnace parameters was difficult since recommended drying, charing, and atomization temperatures and time periods were not applicable to the seawater matrix. The instrumental conditions selected for analysis are given in Table 27.

It was not possible to analyze for lead, copper, cadmium, and nickel by the graphite furnace method. These volatile elements were covolatilized at atomization temperatures required for elimination of the salt matrix. The interference present in this situation precluded analysis by the graphite furnace. Therefore, the APDC-MIBK extraction

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|                          | Ba          | V           | Cr          | Fe          |
|--------------------------|-------------|-------------|-------------|-------------|
| Instrument – HGA         | 2100        | 2100        | 2000        | 2000        |
| Sample Size              | 25µl        | 50µl        | 25µl        | 10µl        |
| Recorder Scale           | X3          | X10         | X3          | X1          |
| Range                    | 2 mV        | 2 mV        | 10 mV       | 10 mV       |
| Wavelength               | 276.5 nm    | 319.25 nm   | 360.9 nm    | 249.0 nm    |
| Slit                     | 3           | 4           | 4           | 3           |
| Source Current           | 25 mA       | 40 mA       | 24 mA       | 26 mA       |
| Dry Temperature          | 150°C       | 150°C       | 230°C       | 125°C       |
| Dry Time                 | 30 sec      | 15 sec      | 40 sec      | 30 sec      |
| Char Temperature         | 1400°C      | 1500°C      | 1350°C      | 1200°C      |
| Char Time                | 30 sec      | 30 sec      | 60 sec      | 30 sec      |
| Atomization Temperature  | 2600°C      | 2700°C      | 2720°C      | 2700°C      |
| Atomization Time         | 8 sec       | 22.5 sec    | 7 sec       | 6 sec       |
| Gas Flow                 | 20/normal   | 50/manual   | 3/manual    | 4/manual    |

Table 27.   Instrumental Conditions of Graphite Furnace for Flameless AAS
Analysis of Seawater.   The HGA-2000 is used in conjunction
with the model 303 AAS unit while the HGA-2100 is used with
the model 306.

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was employed for Pb, Cu, Cd, and Ni analyses of seawater. The volume of water extracted varied since the total volume remaining following flameless analysis was used. The minimum detection limits for cadmium were exceeded for 11 of the 15 samples while lead was detected in only 3 samples.

The refined analysis data for seawater is contained in Appendix C. Statistical treatment for trace metal content measured for seawater is given in Table 28.

The order of decreasing dissolved metal content observed was Fe > Ba > V ≃ Pb > Cr > Cu > Ni > Cd. The trace metal content on sediments varied as follows: Fe > Ba > Cr > V > Ni > Pb > Cu > Cd. The relative ordering is similar for the two types of sample as expected. Chromium and lead demonstrate the most significant difference in the two sample groups.

C. Suspended Particulate Matter

The analysis for barium, vanadium, cadmium, lead, nickel, copper, chromium, and iron content in suspended particulate matter extracts was performed by the flameless graphite furnace AAS technique. Instrumental parameters employed differ from those required for seawater analysis in most cases and are presented in Table 29. The minimum detection limits were exceeded for barium for sample PAD-36 only. The D.L. for vanadium (5 ppb) was exceeded for all of the 15 suspended particulate samples. Statistical analyses of the data is presented in Table 30 for the eight metals determined. The refined computer data is contained in Appendix C.

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| Trace Metal | Average Concentration (ppb) | Standard Deviation (ppb) | Relative Standard Deviation (ppb) |
|---|---|---|---|
| Ba | 43.5 | 22.4 | 51.5 |
| V | 18.7 | 5.2 | 27.8 |
| Cd | 0.05 | 0.03 | 60.0 |
| Pb | 18.3 | 23.0 | 125.3 |
| Ni | 0.75 | 0.63 | 84.0 |
| Cu | 2.6 | 2.5 | 95.8 |
| Cr | 3.4 | 1.2 | 35.3 |
| Fe | 159 | 106 | 66 |

Table 28. Statistical Analysis of Trace Metal Data for Seawater; MAFLA II. The greatest range of sample concentrations was found for lead.

| | Ba | V | Cd | Pb | Ni | Cu | Cr | Fe |
|---|---|---|---|---|---|---|---|---|
| Instrument – HGA | 2100 | 2100 | 2100 | 2000 | 2100 | 2000 | 2000 | 2000 |
| Sample Size | 100µl | 100µl | 25µl | 50µl | 50µl | 50µl | 100µl | 50µl |
| Recorder Scale | X3 | X30 | X1 | X3 | X1 | X1 | X3 | X1 |
| Range | 5 mV | 5 mV | 5 mV | 5 mV | 1 mV | 10 mV | 10 mV | 10 mV |
| Wavelength | 276.5 nm | 319.2 nm | 229.8 nm | 283.1 nm | 232.3 nm | 325.0 nm | 360.9 nm | 283.3 nm |
| Slit | 3 | 4 | 4 | 4 | 3 | 4 | 4 | 4 |
| Source Current | 24 mA | 40 mA | 12 mA | 10 mA | 25 mA | 14 mA | 24 mA | 12 mA |
| Dry Temperature | 120°C | 150°C | 120°C | 150°C | 150°C | 230°C | 230°C | 120°C |
| Dry Time | 30 sec | 40 sec | 30 sec | 30 sec | 30 sec | 30 sec | 40 sec | 30 sec |
| Char Temperature | 1400°C | 1500°C | 380°C | 250°C | 1200°C | 1200°C | 1350°C | 700°C |
| Char Time | 30 sec | 30 sec | 40 sec | 30 sec | 30 sec | 30 sec | 60 sec | 30 sec |
| Atomization Temperature | 2600°C | 2700°C | 2100°C | 2000°C | 2600°C | 2700°C | 2720°C | 2700°C |
| Atomization Time | 8 sec | 17.5 sec | 8 sec | 15 sec | 10 sec | 10 sec | 7 sec | 7 sec |
| Gas Flow | 30/inter.* | 50/auto | 25/inter.* | 3/auto | 30/inter.* | 3/manual | 3/manual | 3/auto |

* Interrupted.

Table 29. Instrumental Conditions of Graphite Furnace for Flameless AAS Analysis Suspended Particulate Matter. The HGA-2000 is uded in conjunction with the model 303 AA unit while the HGA-2100 is used with the model 306.

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| Trace Metal | Average Concentration (ppb) | Standard Deviation (ppb) | Relative Standard Deviation (ppb) |
|---|---|---|---|
| Ba | 9.5 | 6.7 | 70.5 |
| V | < 5 | – | – |
| Cd | 0.73 | 0.55 | 75.5 |
| Pb | 4.9 | 5.2 | 106.0 |
| Ni | 153.1 | 173.9 | 113.6 |
| Cu | 23.0 | 11.5 | 50.3 |
| Cr | 0.58 | 0.22 | 37.3 |
| Fe | 100 | 88 | 88 |

Table 30. Statistical Analysis of Trace Metal Data for Suspended Particulate Matter; MAFLA II. The average concentration of vanadium in the samples was found to be less than the detection limit (5 ppb).

The volume of water filtered during sampling was not supplied to GSRI. Therefore, the data presented is for concentration of trace metal (in parts per billion) in the prepared solution supplied to GSRI. Rigorous interpretation of the data in this form is not possible without additional information.

Significant concentrations of nickel were measured for the suspended particulate matter as compared to the dissolved nickel level. Iron is present in large quantity as expected; however, copper concentration averaged 23.0 ppb versus 2.6 ppb in seawater.

CHAPTER VI


TRACE METAL ANALYSIS OF MAFLA AQUATIC ORGANISM SAMPLES

A.  Sample Preparation

The suspended particulate matter, benthic invertebrate and zoo-
plankton samples were received in the form of acid-extracts of the
original materials.  Approximately ten milliliters of each of the 50
extracts prepared by the prime contractor was delivered to GSRI.  No
information was provided regarding sample weight or dilution volume.
Therefore, the concentration of trace metal in these samples as analyzed
and reported by GSRI represents the amount (parts per billion - ppb)
in the prepared solution.  Conversion of these values to concentration
(ppb) in the actual samples will have to be made either by BLM or the
prime contractor from the sample preparation data supplied by the prime
contractor.  In addition, GSRI was unable to analyze spiked samples or to
make replicate determinations due to the absence of the original samples.
All possible precautions were taken to assure the accuracy of the extract
analyses for trace metal content.  Multiple instrumental calibration
standards were prepared to assure linearity and reproducibility.  Selected
samples were reanalyzed on different days by both of the AAS operators
assigned to the project.  Comparable analytical data were generated by
this additional precautionary measure.

B. Benthic Invertebrates

The 20 benthic invertebrate extracts were analyzed for barium, vanadium, cadmium, lead, nickel, copper, chromium, and iron by flameless AAS. The analysis of this group of extracts was complicated by the presence of undissolved solids in the solutions provided. A white, gelatinous precipitate was found in 62-B, 54-A, and 32-A. This type of precipitate and light yellow translucent chunks were identified in 60-B, and 6-18-II-K-1. Sample 51-A contained a white, powdery precipitate. Sample 49-A had a very low surface tension and a strong, gold color. The precipitates may have formed following initial sample preparation by the prime contractor and could contain metal theoretically leached from the benthic invertebrates. Therefore, GSRI did not filter the extracts. The sample vials were shaken prior to each aliquot removal to attain maximum homogeneity of the same. Repetitive analyses performed in this manner proved to be reproducible. The instrumental parameters used are given in Table 31.

The refined computer analysis is listed in Appendix D for the eight trace metals of interest. Statistical analysis of the refined data is presented in Table 32.

The weight of sample digested and the dilution volume employed were not supplied to GSRI. Therefore, rigorous interpretation of the data, similar to that provided for sediments, is not feasible. Large amounts of iron, nickel and vanadium were found in these extracts, while lead content was quite low.

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| | Ba | V | Cd | Pb | Ni | Cu | Cr | Fe |
|---|---|---|---|---|---|---|---|---|
| Instrument – HGA | 2000 | 2100 | 2100 | 2000 | 2100 | 2000 | 2000 | 2000 |
| Sample Size | 100μl | 10μl | 10μl | 50μl | 25μl | 10μl | 25μl | 50μl |
| Recorder Scale | X1 | X1 | X1 | X1 | X1 | X1 | X1 | X1 |
| Range | 10 mV | 10 mV | 20 mV | 5 mV | 5 mV | 10 mV | 10 mV | 10 mV |
| Wavelength | 277.8 nm | 319.2 nm | 229.8 nm | 283.25 nm | 232.3 nm | 325.0 nm | 360.9 nm | 249.15 nm |
| Slit | 3 | 4 | 4 | 4 | 3 | 4 | 4 | 4 |
| Source Current | 24 mA | 40 mA | 12 mA | 10 mA | 25 mA | 14 mA | 24 mA | 30 mA |
| Dry Temperature | 230°C | 150°C | 120°C | 150°C | 150°C | 230°C | 230°C | 150°C |
| Dry Time | 30 sec | 20 sec | 30 sec | 30 sec | 30 sec | 30 sec | 40 sec | 20 sec |
| Char Temperature | 1400°C | 1500°C | 350°C | 250°C | 1200°C | 1200°C | 1350°C | 1250°C |
| Char Time | 30 sec | 30 sec | 30 sec | 30 sec | 30 sec | 30 sec | 60 sec | 30 sec |
| Atomization Temperature | 2700°C | 2700°C | 2080°C | 2000°C | 2600°C | 2700°C | 2720°C | 2500°C |
| Atomization Time | 10 sec | 17.5 sec | 10 sec | 15 sec | 10 sec | 10 sec | 7 sec | 15 sec |
| Gas Flow | 3/manual | 50/auto | 25/inter.* | 3/auto | 25/normal | 3/manual | 3/manual | 3/manual |

* Interrupted.

Table 31. Instrumental Conditions of Graphite Furnace for Flameless AAS Analysis of Benthic Invertebrates. The HGA-2000 was used in conjunction with the model 303 AA while the HGA-2100 was used with the model 306 unit.

| Trace Metal | Average Concentration (ppb) | Standard Deviation (ppb) | Relative Standard Deviation (ppb) |
|---|---|---|---|
| Ba | 262 | 181 | 69 |
| V | 1656 | 765 | 46 |
| Cd | 179 | 249 | 139 |
| Pb | 22.6 | 24.2 | 107 |
| Ni | 2263 | 5714 | 252 |
| Cu | 247 | 298 | 121 |
| Cr | 82 | 76 | 92 |
| Fe | 15153 | 17883 | 118 |

Table 32. Statistical Analysis of Trace Metal Data for Benthic Invertebrates; MAFLA II. The greatest range of sample concentrations was found for nickel.

## C. Zooplankton

Fifteen zooplankton extracts were analyzed for barium, vanadium, cadmium, lead, nickel, copper, chromium, and iron by the graphite furnace AAS method. The instrumental parameters used throughout these determinations are given in Table 33.

The refined computer calculations are presented in Appendix C. The minimum detection limits were not exceeded for any of the eight elements determined. The statistical analysis of the refined data is given in Table 34. The concentration of copper in zooplankton extracts is similar to that found in benthic invertebrates. Iron is present in the greatest quantity of the eight metals while lead content is the lowest. Barium content was higher than that found in the benthic invertebrate extracts.

|  | Ba | V | Cd | Pb | Ni | Cu | Cr | Fe |
|---|---|---|---|---|---|---|---|---|
| Instrument – HGA | 2000 | 2100 | 2100 | 2000 | 2100 | 2000 | 2000 | 2000 |
| Sample Size | 100μl | 50μl | 10μl | 50μl | 25μl | 10μl | 25μl | 10μl |
| Recorder Scale | X1 | X1 | X1 | X1 | X1 | X1 | X3 | X1 |
| Range | 10 mV | 10 mV | 20 mV | 5 mV | 1 mV | 10 mV | 10 mV | 10 mV |
| Wavelength | 277.8 nm | 319.2 nm | 229.8 nm | 283.25 nm | 232.3 nm | 325.0 nm | 360.9 nm | 249.0 nm |
| Slit | 3 | 4 | 4 | 4 | 3 | 4 | 4 | 3 |
| Source Current | 24 mA | 40 mA | 12 mA | 10 mA | 25 mA | 14 mA | 24 mA | 26 mA |
| Dry Temperature | 230°C | 150°C | 120°C | 150°C | 150°C | 230°C | 230°C | 150°C |
| Dry Time | 30 sec | 20 sec | 30 sec | 30 sec | 30 sec | 30 sec | 40 sec | 30 sec |
| Char Temperature | 1400°C | 1500°C | 380°C | 250°C | 1200°C | 1200°C | 1350°C | 1100°C |
| Char Time | 30 sec | 30 sec | 40 sec | 30 sec | 30 sec | 30 sec | 60 sec | 30 sec |
| Atomization Temperature | 2700°C | 2700°C | 2100°C | 2000°C | 2600°C | 2700°C | 2720°C | 2500°C |
| Atomization Time | 10 sec | 17.5 sec | 8 sec | 15 sec | 10 sec | 10 sec | 7 sec | 6 sec |
| Gas Flow | 3/manual | 50/manual | 25/inter.* | 3/auto | 30/inter.* | 3/manual | 3/manual | 5/manual |

* Interrupted.

Table 33. Instrumental Conditions of Graphite Furnace for Flameless AAS Analysis of Zooplankton. The HGA 2000 was used in conjunction with the model 303 AA while the HGA-2100 was used with the model 306.

| Trace Metal | Average Concentration (ppb) | Standard Deviation (ppb) | Relative Standard Deviation (ppb) |
|---|---|---|---|
| Ba | 607 | 446 | 73.5 |
| V | 48 | 27 | 56.8 |
| Cd | 88 | 83 | 94 |
| Pb | 8.0 | 3.1 | 38.2 |
| Ni | 178 | 67 | 38 |
| Cu | 224 | 129 | 57.4 |
| Cr | 21.2 | 22.5 | 106 |
| Fe | 4138 | 5696 | 138 |

Table 34. Statistical Analysis of Trace Metal Data for Zooplankton; MAFLA II. The greatest range of sample concentrations was observed for iron.

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APPENDICES

APPENDIX A

PROCEDURES

APPENDIX A


Environmental Protection Agency
Region IV, Surveillance & Analysis Division
Chemical Services Branch

Tentative Digestion of Sediments for Metal Analysis
June 28, 1973


1. Weigh 1-2 g of dry ($103^{o}C$) sediment into a 250 ml erlenmeyer
   flask.

2. Add 50 ml of water, 0.5 ml conc. $HNO_3$ and 5 ml conc. HCl.

3. Heat at $95^{o}$ for 15 minutes.

4. Cool and clarify the sample by filtering or centrifuging.

5. Dilute to 100 ml.

6. Proceed with atomic absorption analyses for Pb, Zn, Mn, Cd, Cu,
   Ni, and Cr.


GSRI Alterations[*]


1. 4 g of dry sediment was used.

2. 100 ml of water, 1.0 ml conc. $HNO_3$, and 10 ml conc. HCl were added.

4. Filtration rather than centrifugation was performed.

5. The final dilution volume was 50 ml.


[*]
 Changes described were effected in order to improve minimum
    detection limits.

APPENDIX B

B.  REFINED TRACE METAL DATA FOR MAFLA SEDIMENT SAMPLES

    1.  Detection Limits

    (All results expressed in ppm on a dry weight basis)

APPENDIX B

Standard __Aqueous__

| BLM SAMPLE I.D. | GSRI SAMPLE I.D. | a ≠ | b ≠ |
|---|---|---|---|
| 1 | 1-1 | 15.8 | 12.6 |
| 2 | 2-2 | 0 | 0 |
| 3 | 3-3 | 51.1 | 19.1 |
| 5 | 5-4 | 47.1 | 31.8 |
| 6 | 6-5 | 42.5 | 31.6 |
| 7 | 7-6 | 34.2 | 31.1 |
| 9 | 9-7 | 21.7 | 20.5 |
| 11 | 11-8 | 14.3 | 18.3 |
| 13 | 13-9 | 29.9 | 29.1 |
| 16 | 16-10 | 33.0 | 31.5 |
| 19 | 19-11 | 26.4 | 20.5 |
| 22 | 22-12 | 23.6 | 17.4 |
| 24 | 24-13 | 23.2 | |
| 25 | 25-14 | 36.9 | 17.3 |
| 26 | 26-15 | 16.8 | 36.7 |
| 27 | 27-16 | 46.7 | 36.7 |
| 28 | 28-17 | 22.5 | 16.0 |
| 29 | 29-18 | 16.6 | 17.2 |
| 30 | 30-19 | 6.5 | 5.3 |
| 32 | 32-20 | 19.9 | 17.2 |
| 33 | 33-21 | 21.9 | 14.9 |
| 34 | 34-22 | 16.1 | 21.7 |
| 36 | 36-23 | 6.4 | 6.6 |
| 38 | 38-24 | 4.7 | 4.6 |
| 39 | 39-25 | 21.2 | 24.9 |
| 41 | 41-26 | 19.8 | 17.3 |
| 42 | 42-27 | 9.8 | 7.7 |
| 44 | 44-28 | 9.9 | 9.2 |
| 48 | 48-29 | 20.5 | 24.5 |
| 49 | 49-30 | 26.9 | 36.9 |
| 54 | 54-31 | 40.8 | 44.2 |
| 56 | 56-32 | 17.9 | 27.2 |
| 57 | 57-33 | 18.9 | |
| 60 | 60-34 | | 18.5 |
| 63 | 63-35 | 18.0 | 25.9 |

* Analyzed by Flameless AAS

≠ Values corrected for % recovery from SRM sediments

| BLM SAMPLE I.D. | GSRI SAMPLE I.D. | a | b |
|---|---|---|---|
| 1 | 1-1 | 14.5 | 13.4 |
| 2 | 2-2 | <D.L.* | <D.L.* |
| 3 | 3-3 | 5.6 | 4.6 |
| 5 | 5-4 | 15.6 | 10.6 |
| 6 | 6-5 | 7.8 | 8.8 |
| 7 | 7-6 | | 7.4 |
| 9 | 9-7 | 8.7 | 3.8 |
| 11 | 11-8 | 1.7 | 2.1 |
| 13 | 13-9 | 14.4 | 5.9 |
| 16 | 16-10 | 9.2 | 7.2 |
| 19 | 19-11 | 7.1 | 5.4 |
| 22 | 22-12 | 10.2 | 8.7 |
| 24 | 24-13 | 5.9 | |
| 25 | 25-14 | 12.4 | 9.1 |
| 26 | 26-15 | 31.8 | 26.1 |
| 27 | 27-16 | 22.8 | 25.0 |
| 28 | 28-17 | 5.9 | 7.5 |
| 29 | 29-18 | 14.0 | 13.2 |
| 30 | 30-19 | 1.4 | 3.3 |
| 32 | 32-20 | 5.8 | |
| 33 | 33-21 | 7.1 | 8.3 |
| 34 | 34-22 | 13.4 | 11.7 |
| 36 | 36-23 | 3.2 | 3.7 |
| 38 | 38-24 | 2.0 | 2.8 |
| 39 | 39-25 | 8.9 | 12.8 |
| 41 | 41-26 | 33.2 | 29.4 |
| 42 | 42-27 | 5.0 | 7.3 |
| 44 | 44-28 | 14.4 | 15.8 |
| 48 | 48-29 | 22.3 | 24.6 |
| 49 | 49-30 | 30.8 | 31.7 |
| 54 | 54-31 | 119 | 124 |
| 56 | 56-32 | 10.4 | 9.0 |
| 57 | 57-33 | 8.2 | |
| 60 | 60-34 | | 6.4 |
| 63 | 63-35 | 6.9 | 8.7 |

* Less than minimum detection limit (0.6 ppm).

| BLM SAMPLE I.D. | GSRI SAMPLE I.D. | a | b |
|---|---|---|---|
| 1 | 1-1 | 11.7 | 11.0 |
| 2 | 2-2 | <D.L.* | <D.L.* |
| 3 | 3-3 | 4.6 | 3.8 |
| 5 | 5-4 | 12.8 | 8.7 |
| 6 | 6-5 | 6.4 | 7.2 |
| 7 | 7-6 | | 6.1 |
| 9 | 9-7 | 7.2 | 3.1 |
| 11 | 11-8 | 1.4 | 1.8 |
| 13 | 13-9 | 11.8 | 4.9 |
| 16 | 16-10 | 7.6 | 5.9 |
| 19 | 19-11 | 5.9 | 4.5 |
| 22 | 22-12 | 8.4 | 7.2 |
| 24 | 24-13 | 4.9 | |
| 25 | 25-14 | 10.2 | 7.4 |
| 26 | 26-15 | 26.2 | 21.6 |
| 27 | 27-16 | 18.7 | 20.6 |
| 28 | 28-17 | 4.8 | 6.1 |
| 29 | 29-18 | 11.6 | 10.9 |
| 30 | 30-19 | 1.1 | 2.7 |
| 32 | 32-20 | 4.8 | |
| 33 | 33-21 | 5.8 | 6.8 |
| 34 | 34-22 | 11.0 | 9.6 |
| 36 | 36-23 | 2.6 | 3.0 |
| 38 | 38-24 | 1.7 | 2.3 |
| 39 | 39-25 | 7.3 | 10.6 |
| 41 | 41-26 | 27.3 | 24.3 |
| 42 | 42-27 | 4.2 | 5.9 |
| 44 | 44-28 | 11.8 | 13.0 |
| 48 | 48-29 | 18.3 | 20.2 |
| 49 | 49-30 | 25.4 | 26.1 |
| 54 | 54-31 | 98 | 102 |
| 56 | 56-32 | 8.6 | 7.4 |
| 57 | 57-33 | 6.8 | |
| 60 | 60-34 | | 5.3 |
| 63 | 63-35 | 5.7 | 7.1 |

* Less than detection limit 0.6 ppm.

| BLM SAMPLE I.D. | GSRI SAMPLE I.D. | a | b |
|---|---|---|---|
| 1 | 1-1 | 0.02 | |
| 2 | 2-2 | 0.07 | 0.02 |
| 3 | 3-3 | 0.05 | 0.16 |
| 5 | 5-4 | 0.19 | 0.28 |
| 6 | 6-5 | 0.10 | 0.06 |
| 7 | 7-6 | 0.04 | 0.07 |
| 9 | 9-7 | 0.12 | 0.07 |
| 11 | 11-8 | 0.04 | 0.07 |
| 13 | 13-9 | 0.11 | 0.11 |
| 16 | 16-10 | 0.09 | 0.06 |
| 19 | 19-11 | 0.09 | 0.12 |
| 22 | 22-12 | 0.07 | 0.05 |
| 24 | 24-13 | 0.10 | 0.07 |
| 25 | 25-14 | 0.11 | 0.11 |
| 26 | 26-15 | 0.07 | 0.09 |
| 27 | 27-16 | 0.16 | 0.17 |
| 28 | 28-17 | 0.09 | 0.03 |
| 29 | 29-18 | 0.12 | 0.16 |
| 30 | 30-19 | 0.05 | 0.03 |
| 32 | 32-20 | 0.07 | 0.08 |
| 33 | 33-21 | 0.12 | 0.12 |
| 34 | 34-22 | 0.14 | 0.16 |
| 36 | 36-23 | 0.08 | 0.08 |
| 38 | 38-24 | 0.03 | 0.03 |
| 39 | 39-25 | 0.09 | 0.15 |
| 41 | 41-26 | 0.02 | 0.05 |
| 42 | 42-27 | 0.08 | 0.03 |
| 44 | 44-28 | 0.02 | 0.05 |
| 48 | 48-29 | 0.09 | 0.14 |
| 49 | 49-30 | 0.09 | 0.12 |
| 54 | 54-31 | 0.08 | 0.08 |
| 56 | 56-32 | 0.02 | 0.06 |
| 57 | 57-33 | 0.08 | 0.05 |
| 60 | 60-34 | 0.09 | 0.05 |
| 63 | 63-35 | 0.07 | 0.08 |

* Analyzed by Flameless AAS

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| BLM SAMPLE I.D. | GSRI SAMPLE I.D. | a | b |
|---|---|---|---|
| 1 | 1-1 | | 4.8 |
| 2 | 2-2 | 4.0 | 5.6 |
| 3 | 3-3 | | 6.5 |
| 5 | 5-4 | 6.4 | 3.8 |
| 6 | 6-5 | 5.4 | 2.2 |
| 7 | 7-6 | | 1.7 |
| 9 | 9-7 | | 2.4 |
| 11 | 11-8 | 7.6 | 7.2 |
| 13 | 13-9 | 5.7 | 5.3 |
| 16 | 16-10 | 4.5 | 2.7 |
| 19 | 19-11 | 4.8 | 3.0 |
| 22 | 22-12 | 6.0 | 3.5 |
| 24 | 24-13 | 2.5 | 2.1 |
| 25 | 25-14 | 5.3 | 3.3 |
| 26 | 26-15 | 9.5 | 13.4 |
| 27 | 27-16 | 7.3 | 5.5 |
| 28 | 28-17 | 3.5 | 4.8 |
| 29 | 29-18 | 5.7 | 5.6 |
| 30 | 30-19 | 3.0 | 3.0 |
| 32 | 32-20 | 3.8 | 4.5 |
| 33 | 33-21 | 5.1 | 5.4 |
| 34 | 34-22 | 5.5 | 5.3 |
| 36 | 36-23 | 5.9 | 5.3 |
| 38 | 38-24 | 4.5 | 2.9 |
| 39 | 39-25 | 4.5 | 4.1 |
| 41 | 41-26 | 7.9 | 5.3 |
| 42 | 42-27 | 2.4 | 2.8 |
| 44 | 44-28 | 7.9 | |
| 48 | 48-29 | 4.4 | 4.0 |
| 49 | 49-30 | 6.4 | 2.0 |
| 54 | 54-31 | 3.8 | 4.2 |
| 56 | 56-32 | 3.5 | 5.5 |
| 57 | 57-33 | 3.2 | 3.8 |
| 60 | 63-35 | 2.5 | |
| 63 | 63-35 | 2.3 | 3.4 |

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| BLM SAMPLE I.D. | GSRI SAMPLE I.D. | a | b |
|---|---|---|---|
| 1 | 1-1 | 5.4 | 5.8 |
| 2 | 2-2 | 43.9* | 45.7* |
| 3 | 3-3 | 12.3 | 12.9 |
| 5 | 5-4 | 6.0 | 8.1 |
| 6 | 6-5 | 2.2 | 1.8 |
| 7 | 7-6 | 3.2 | 2.8 |
| 9 | 9-7 | 1.3 | 3.0 |
| 11 | 11-8 | 3.9 | 4.4 |
| 13 | 13-9 | 6.4 | 7.5 |
| 16 | 16-10 | 8.4 | 5.8 |
| 19 | 19-11 | 5.4 | 5.2 |
| 22 | 22-12 | 4.9 | 7.6 |
| 24 | 24-13 | 0.3 | 0.3 |
| 25 | 25-14 | 3.9 | 2.3 |
| 26 | 26-15 | 9.6 | 13.5 |
| 27 | 27-16 | 9.8 | 11.6 |
| 28 | 28-17 | 6.7 | 8.6 |
| 29 | 29-18 | 9.0 | 8.8 |
| 30 | 30-19 | 1.8 | 1.5 |
| 32 | 32-20 | 7.9 | 5.4 |
| 33 | 33-21 | 4.7 | 3.1 |
| 34 | 34-22 | 8.3 | 6.9 |
| 36 | 36-23 | 2.3 | 2.0 |
| 38 | 38-24 | 1.7 | 1.6 |
| 39 | 39-25 | 9.1 | 8.0 |
| 41 | 41-26 | 12.8 | 12.6 |
| 42 | 42-27 | 2.9 | 4.5 |
| 44 | 44-28 | 7.7 | 4.6 |
| 48 | 48-29 | 7.6 | 9.0 |
| 49 | 49-30 | 9.3 | 11.5 |
| 54 | 54-31 | 12.1 | 17.2 |
| 56 | 56-32 | 5.0 | 5.6 |
| 57 | 57-33 | 2.3 | 2.7 |
| 60 | 60-34 | 3.6 | 4.0 |
| 63 | 63-35 | 1.7 | 6.7 |

* Insufficient sample quantity; no $CaCO_3$ (different matrix); nonabsorbing wavelength calculated from composite including this sample; required dilution for analysis, i.e. error for this sample is significantly greater than for remaining 34 samples.

| BLM SAMPLE I.D. | GSRI SAMPLE I.D. | a | b |
|---|---|---|---|
| 1 | 1-1 | 5.9 | 6.6 |
| 2 | 2-2 | * | * |
| 3 | 3-3 | 13.3 | 13.9 |
| 5 | 5-4 | 6.4 | 9.1 |
| 6 | 6-5 | 2.7 | 2.0 |
| 7 | 7-6 | 3.5 | 3.1 |
| 9 | 9-7 | 1.4 | 3.4 |
| 11 | 11-8 | 4.2 | 4.8 |
| 13 | 13-9 | 7.0 | 8.1 |
| 16 | 16-10 | 9.4 | 6.8 |
| 19 | 19-11 | 6.0 | 5.7 |
| 22 | 22-12 | 5.3 | 8.6 |
| 24 | 24-13 | 0.3 | 0.3 |
| 25 | 25-14 | 4.2 | 2.6 |
| 26 | 26-15 | 10.4 | 14.4 |
| 27 | 27-16 | 11.2 | 13.2 |
| 28 | 28-17 | 7.6 | 9.8 |
| 29 | 29-18 | 10.2 | 10.0 |
| 30 | 30-19 | 2.0 | 1.8 |
| 32 | 32-20 | 9.0 | 6.2 |
| 33 | 33-21 | 5.4 | 3.6 |
| 34 | 34-22 | 9.5 | 7.9 |
| 36 | 26-23 | 2.7 | 2.3 |
| 38 | 38-24 | 2.0 | 1.8 |
| 39 | 39-25 | 10.5 | 8.5 |
| 41 | 41-26 | 14.6 | 14.4 |
| 42 | 42-27 | 3.4 | 5.2 |
| 44 | 44-28 | 8.8 | 5.2 |
| 48 | 48-29 | 8.6 | 10.3 |
| 49 | 49-30 | 10.6 | 13.1 |
| 54 | 54-31 | 13.8 | 19.6 |
| 56 | 56-32 | 5.4 | 6.5 |
| 57 | 57-33 | 2.6 | 3.0 |
| 60 | 60-34 | 3.9 | 4.6 |
| 63 | 63-35 | 1.9 | 7.6 |

* Insufficient sample quantity; no $CaCO_3$ (different matrix); nonabsorbing wavelength calculated from composite including this sample; required dilution for analysis, i.e. error for this sample is significantly greater than for remaining 34 samples.

| BLM SAMPLE I.D. | GSRI SAMPLE I.D. | a | b |
|---|---|---|---|
| 1 | 1-1 | 2.5 | 1.3 |
| 2 | 2-2 | | 2.4 |
| 3 | 3-3 | 2.9 | 2.2 |
| 5 | 5-4 | 1.2 | 0.8 |
| 6 | 6-5 | 1.2 | 0.5 |
| 7 | 7-6 | | 0.8 |
| 9 | 9-7 | 1.2 | |
| 11 | 11-8 | 3.0 | 2.8 |
| 13 | 13-9 | 4.0 | 3.2 |
| 16 | 16-10 | 0.5 | 0.2 |
| 19 | 19-11 | 0.5 | 0.5 |
| 22 | 22-12 | 2.7 | 2.2 |
| 24 | 24-13 | 0.5 | |
| 25 | 25-14 | 1.0 | |
| 26 | 26-15 | 8.6 | 9.0 |
| 27 | 27-16 | 1.3 | 1.6 |
| 28 | 28-17 | 0.8 | 0.2 |
| 29 | 29-18 | 2.2 | 1.5 |
| 30 | 30-19 | 0.5 | 0.2 |
| 32 | 32-20 | 1.1 | 0.6 |
| 33 | 33-21 | 0.4 | |
| 34 | 34-22 | 2.8 | 1.9 |
| 36 | 26-23 | 0.3 | 0.4 |
| 38 | 38-24 | | 0.2 |
| 39 | 39-25 | 2.0 | 1.8 |
| 41 | 41-26 | 5.0 | 4.6 |
| 42 | 42-27 | 3.9 | 0.4 |
| 44 | 44-28 | 2.2 | 1.9 |
| 48 | 48-29 | 1.3 | |
| 49 | 49-30 | 2.3 | 2.6 |
| 54 | 54-31 | 132.2 | 127.0 |
| 56 | 56-32 | 0.8 | |
| 57 | 57-33 | 0.4 | |
| 60 | 60-34 | 0.5 | |
| 63 | 63-35 | 0.5 | |

Trace Metal ___Cu___

Standard ___Matrix___

| BLM SAMPLE I.D. | GSRI SAMPLE I.D. | a | b |
|---|---|---|---|
| 1 | 1-1 | 2.9 | 1.5 |
| 2 | 2-2 | | |
| 3 | 3-3 | 3.4 | 2.5 |
| 5 | 5-4 | 1.5 | 0.9 |
| 6 | 6-5 | 1.5 | 0.6 |
| 7 | 7-6 | | 0.9 |
| 9 | 9-7 | 1.5 | |
| 11 | 11-8 | 3.6 | 3.3 |
| 13 | 13-9 | 4.6 | 3.8 |
| 16 | 16-10 | 0.6 | 0.4 |
| 19 | 19-11 | 0.7 | 0.6 |
| 22 | 22-12 | 3.3 | 2.5 |
| 24 | 24-13 | 0.7 | |
| 25 | 25-14 | 1.3 | |
| 26 | 26-15 | 9.9 | 10.5 |
| 27 | 27-16 | 1.6 | 1.8 |
| 28 | 28-17 | 0.9 | 0.3 |
| 29 | 29-18 | 2.6 | 1.7 |
| 30 | 30-19 | 0.6 | 0.4 |
| 32 | 32-20 | 1.3 | 0.8 |
| 33 | 33-21 | 0.5 | |
| 34 | 34-22 | 3.4 | 2.2 |
| 36 | 26-23 | 0.4 | 0.6 |
| 38 | 38-24 | | 0.3 |
| 39 | 39-25 | 2.2 | 2.2 |
| 41 | 41-26 | 5.8 | 5.4 |
| 42 | 42-27 | 4.5 | |
| 44 | 44-28 | 2.6 | 2.2 |
| 48 | 48-29 | 1.5 | |
| 49 | 49-30 | 2.6 | 3.1 |
| 54 | 54-31 | 152.3 | 146.5 |
| 56 | 56-32 | 0.9 | 1.2 |
| 57 | 57-33 | 0.5 | |
| 60 | 60-34 | 0.5 | |
| 63 | 63-35 | 0.6 | |

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| BLM SAMPLE I.D. | GSRI SAMPLE I.D. | a | b |
|---|---|---|---|
| 1 | 1-1 | 12.4 | 11.9 |
| 2 | 2-2 | 17.1 | 14.1 |
| 3 | 3-3 | 34.4 | 7.6 |
| 5 | 5-4 | 21.5 | 19.6 |
| 6 | 6-5 | 12.7 | 12.8 |
| 7 | 7-6 | 23.0 | 15.9 |
| 9 | 9-7 | 16.0 | 12.2 |
| 11 | 11-8 | 14.7 | 3.3 |
| 13 | 13-9 | 17.5 | 19.4 |
| 16 | 16-10 | 19.8 | 20.0 |
| 19 | 19-11 | 14.0 | 14.4 |
| 22 | 22-12 | 16.9 | 15.7 |
| 24 | 24-13 | 10.5 | 6.1 |
| 25 | 25-14 | 17.5 | 16.3 |
| 26 | 26-15 | 31.1 | 54.0 |
| 27 | 27-16 | 19.7 | 18.3 |
| 28 | 28-17 | 13.3 | 10.8 |
| 29 | 29-18 | 19.0 | 16.4 |
| 30 | 30-19 | 2.4 | 2.1 |
| 32 | 32-20 | 17.6 | 13.6 |
| 33 | 33-21 | 13.3 | 10.9 |
| 34 | 34-22 | 15.3 | 13.6 |
| 36 | 26-23 | 3.5 | 2.9 |
| 38 | 38-24 | 3.1 | 2.7 |
| 39 | 39-25 | 20.2 | 18.7 |
| 41 | 41-26 | 31.2 | 25.4 |
| 42 | 42-27 | 12.7 | 10.7 |
| 44 | 44-28 | 11.6 | 11.6 |
| 48 | 48-29 | 16.5 | 14.5 |
| 49 | 49-30 | 20.9 | 19.3 |
| 54 | 54-31 | 17.4 | 16.0 |
| 56 | 56-32 | 15.3 | 13.4 |
| 57 | 57-33 | 16.0 | 13.6 |
| 60 | 60-34 | 11.9 | 10.3 |
| 63 | 63-35 | 12.9 | 10.6 |

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| BLM<br>SAMPLE<br>I.D. | GSRI<br>SAMPLE<br>I.D. | a | b |
|---|---|---|---|
| 1 | 1-1 | 11.1 | 10.6 |
| 2 | 2-2 | 15.1 | 12.4 |
| 3 | 3-3 | 30.9 | 6.7 |
| 5 | 5-4 | 19.2 | 17.5 |
| 6 | 6-5 | 11.3 | 11.4 |
| 7 | 7-6 | 20.6 | 14.2 |
| 9 | 9-7 | 14.3 | 10.9 |
| 11 | 11-8 | 13.1 | 2.9 |
| 13 | 13-9 | 15.6 | 17.4 |
| 16 | 16-10 | 17.7 | 17.9 |
| 19 | 19-11 | 12.4 | 12.8 |
| 22 | 22-12 | 15.1 | 14.0 |
| 24 | 24-13 | 9.4 | 16.0 |
| 25 | 25-14 | 15.6 | 16.3 |
| 26 | 26-15 | 25.6 | 48.4 |
| 27 | 27-16 | 17.7 | 16.4 |
| 28 | 28-17 | 11.8 | 9.6 |
| 29 | 29-18 | 16.6 | 14.3 |
| 30 | 30-19 | 2.0 | 1.7 |
| 32 | 32-20 | 15.6 | 12.0 |
| 33 | 33-21 | 11.5 | 9.4 |
| 34 | 34-22 | 13.3 | 11.8 |
| 36 | 26-23 | 3.0 | 2.5 |
| 38 | 38-24 | 2.6 | 2.3 |
| 39 | 39-25 | 18.0 | 16.7 |
| 41 | 41-26 | 27.7 | 22.6 |
| 42 | 42-27 | 11.1 | 9.4 |
| 44 | 44-28 | 10.1 | 10.1 |
| 48 | 48-29 | 14.1 | 12.4 |
| 49 | 49-30 | 18.0 | 16.6 |
| 54 | 54-31 | 15.0 | 13.8 |
| 56 | 56-32 | 13.2 | 11.7 |
| 57 | 57-33 | 13.6 | 15.5 |
| 60 | 60-34 | 10.3 | 8.9 |
| 63 | 63-35 | 11.1 | 9.1 |

| BLM SAMPLE I.D. | GSRI SAMPLE I.D. | a | b |
|---|---|---|---|
| 1 | 1-1 | 6850 | 5570 |
| 2 | 2-2 | 2310 | 2300 |
| 3 | 3-3 | 2280 | 2090 |
| 5 | 5-4 | 6640 | 5330 |
| 6 | 6-5 | 1120 | 870 |
| 7 | 7-6 | 1190 | 1060 |
| 9 | 9-7 | 4880 | 2660 |
| 11 | 11-8 | 10300 | 10220 |
| 13 | 13-9 | 5620 | 5340 |
| 16 | 16-10 | 2660 | 2040 |
| 19 | 19-11 | 3720 | 3340 |
| 22 | 22-12 | 4220 | 3670 |
| 24 | 24-13 | 780 | 740 |
| 25 | 25-14 | 4760 | 4370 |
| 26 | 26-15 | 14370 | 13310 |
| 27 | 27-16 | 10090 | 12420 |
| 28 | 28-17 | 590 | 550 |
| 29 | 29-18 | 6650 | 6740 |
| 30 | 30-19 | 470 | 550 |
| 32 | 32-20 | 4650 | 4910 |
| 33 | 33-21 | 1110 | 1130 |
| 34 | 34-22 | 1770 | 1750 |
| 36 | 26-23 | 870 | 920 |
| 38 | 38-24 | 660 | 600 |
| 39 | 39-25 | 6900 | 6100 |
| 41 | 41-26 | 12020 | 11880 |
| 42 | 42-27 | 3530 | 3390 |
| 44 | 44-28 | 6190 | 6190 |
| 48 | 48-29 | 10660 | 8470 |
| 49 | 49-30 | 14540 | 15120 |
| 54 | 54-31 | 18280 | 17210 |
| 56 | 56-32 | 1570 | 1510 |
| 57 | 57-33 | 1450 | 1700 |
| 60 | 60-34 | 960 | 900 |
| 63 | 63-35 | 940 | 850 |

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APPENDIX B 1


Experimentally Determined

Minimum Detection Limits (DL) for Trace Metal Assay of Sediments

| Trace Metal | Instrumental DL (ppm) | Sample DL (ppm) |
|---|---|---|
| Ba | 0.005 | 0.06 |
| V | 0.05 | 0.62 |
| Cd | 0.001 | 0.01 |
| Pb | 0.05 | 0.62 |
| Ni ($N_2O$ - $C_2H_2$) | 0.02 | 0.25 |
| Ni (Air - $C_2H_2$) | 0.006 | 0.08 |
| Cu | 0.003 | 0.04 |
| Cr ($N_2O$ - $C_2H_2$) | 0.1 | 1.25 |
| Cr (Air - $C_2H_2$) | 0.005 | 0.06 |
| Fe | 0.005 | 0.06 |

APPENDIX C

C.  REFINED TRACE METAL DATA FOR MAFLA  SEAWATER SAMPLES

1.  Dissolved Metals

   a.  Detection Limits

2.  Suspended Metals

   (All results expressed in ppb)

| BLM Sample No. | GSRI Sample No. | BLM Data Sheet for Trace Metal Concentration in Filtered Sea Water | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Ba | V | Cd | Pb | Ni | Cu | Cr | Fe |
| TM-363 | TM-363-1 | 25 | 14.2 | < .03 | <0.2 | 0.20 | 0.99 | 2.4 | 145 |
| TM-366 | TM-366-2 | 42 | 22.7 | 0.03 | <0.2 | 0.48 | 1.92 | 2.9 | 212 |
| TM-527 | TM-527-3 | 46 | 25.3 | <0.03 | <0.2 | 0.43 | 3.76 | 2.0 | 35 |
| TM-530 | TM-530-4 | 50 | 24.9 | <0.03 | <0.2 | 0.79 | 4.51 | 3.0 | 45 |
| TM-535 | TM-535-5 | 77 | 29.3 | <0.03 | <0.2 | 0.92 | 6.75 | 2.8 | 55 |
| TM-880 | TM-880-6 | 51 | 17.3 | <0.03 | <0.2 | 2.77 | 2.21 | 6.0 | 117 |
| TM-889 | TM-889-7 | 36 | 16.0 | 0.09 | 2.09 | 1.18 | 4.31 | 3.3 | 120 |
| TM-891 | TM-891-8 | 53 | 19.4 | <0.03 | <0.2 | 0.78 | 1.89 | 4.3 | 185 |
| TM-909 | TM-909-9 | 25 | 20.0 | <0.03 | <0.2 | 0.77 | 8.62 | 2.5 | 290 |
| TM-917 | TM-917-10 | 15 | 14.8 | <0.03 | <0.2 | 0.21 | 0.82 | 2.5 | 172 |
| TM-920 | TM-920-11 | 11 | 13.2 | <0.03 | <0.2 | 0.56 | 0.93 | 2.6 | 110 |
| TM-921 | TM-921-12 | 21 | 11.2 | <0.03 | <0.2 | 0.23 | 0.52 | 4.1 | 425 |
| TM-922 | TM-922-13 | 42 | 19.6 | 0.06 | 34.55 | 0.69 | 0.65 | 5.7 | 45 |
| TM-924 | TM-924-14 | 79 | 13.5 | <0.03 | <0.2 | 0.74 | 0.89 | 3.4 | 232 |
| TM-925 | TM-925-15 | 80 | 18.9 | 0.03 | <0.2 | 0.42 | 0.32 | 3.9 | 195 |

APPENDIX C 1a

Experimentally Determined Minimum Detection

Limits (DL) For Trace Metal Analysis By

Flameless AAS (Dissolved Metals in Water)

| Trace Metal | Instrumental DL (ppb)[1] | Perkin-Elmer DL (ppb)[2] |
|---|---|---|
| Ba | 3 | 6 |
| V | 5 | 7 |
| Cd | 0.03 | 0.02 |
| Pb | 0.2 | 0.2 |
| Ni | 3.5 | 2.8 |
| Ca | 0.2 | 1 |
| Cr | 0.3 | 0.5 |
| Fe | 0.5 | 0.6 |

[1] DL based on sample injection size of 50 μl

[2] Analytical Methods Using the HGA Graphite Furnace

| BLM Sample No. | GSRI Sample No. | Ba | V | Cd | Pb | Ni | Cu | Cr | Fe |
|---|---|---|---|---|---|---|---|---|---|
| | | BLM Data Sheet for Trace Metal Concentrations in 10 ml. Acid Extracts of Suspended Particulate Matter | | | | | | | |
| PAD-7 | PAD-7-1 | 4.5 | < 5 | 2.2 | 20.0 | 67 | 19.0 | 1.03 | 168 |
| PAD-11 | PAD-11-2 | 21 | < 5 | 0.87 | 5.0 | 39 | 62.5 | 0.62 | 44 |
| PAD-13 | PAD-13-3 | 4 | < 5 | 0.65 | 3.5 | 56 | 19.5 | 0.80 | 247 |
| PAD-14 | PAD-14-4 | 7 | < 5 | 0.45 | 7.7 | 106 | 22.0 | 0.74 | 284 |
| PAD-25 | PAD-25-5 | 7 | < 5 | 0.77 | 5.5 | 80 | 22.0 | 0.60 | 113 |
| PAD-36 | PAD-36-6 | 3 | < 5 | 0.45 | 12.8 | 310 | 17.0 | 0.50 | 146 |
| PAD-45 | PAD-45-7 | 12 | < 5 | 0.38 | 1.6 | 25 | 17.5 | 0.42 | 22 |
| PAD-61 | PAD-61-8 | 11 | < 5 | 0.30 | 1.0 | 112 | 28.5 | 0.40 | 23 |
| PAD-66 | PAD-66-9 | 6 | < 5 | 0.40 | 2.0 | 350 | 21.0 | 0.36 | 96 |
| PAD-67 | PAD-67-10 | 11 | < 5 | 0.25 | 3.6 | 98 | 26.5 | 0.96 | 193 |
| PAD-76 | PAD-76-11 | 5 | < 5 | 0.55 | 2.5 | 600 | 22.0 | 0.41 | 26 |
| PAD-77 | PAD-77-12 | 5 | < 5 | 0.25 | 1.7 | 19 | 17.0 | 0.54 | 12 |
| PAD-84 | PAD-84-13 | 10 | < 5 | 0.75 | 1.5 | 48 | 13.0 | 0.56 | 47 |
| PAD-85 | PAD-85-14 | <3 | < 5 | 1.70 | 3.0 | 380 | 18.0 | 0.51 | 52 |
| PAD-87 | PAD-87-15 | 26 | < 5 | 1.05 | 2.0 | 7 | 20.0 | 0.29 | 28 |

APPENDIX D

D.  REFINED TRACE METAL DATA FOR MAFLA AQUATIC ORGANISM SAMPLES


1.  Benthic Invertebrates

2.  Zooplankton

BLM Data Sheet for Trace Metal Concentrations in
Benthic Inverterbrates as calculated from GSRI &
SUSIO data.   (MAFLA baseline report,) concentration in ppm.

| BLM Sample No. | Ba | V | Cd | Pb | Ni | Cu | Cr | Fe |
|---|---|---|---|---|---|---|---|---|
| 62E | 13.9 | 73.7 | 1.2 | .894 | 20.9 | 3.03 | 6.58 | 818. |
| 62B | 8.55 | 76.3 | 26.0 | 2.07 | 815. | 5.26 | 7.46 | 1867. |
| 62-A-1 | 19.9 | 73.0 | 15.9 | 2.54 | 46.2 | 7.86 | 5.50 | 781. |
| 60-B | 7.84 | 153. | .4 | .64 | 57.0 | 19.2 | 0.6 | 198. |
| 60-A | 9.58 | 171. | 42.8 | 1.09 | 396. | 11.5 | 3.2 | 781. |
| 6-18-II-K-1 | 21.2 | 110. | .79 | 1.32 | 5.41 | 2.5 | 6.30 | 975. |
| 51-F | 7.38 | 90.0 | 9.35 | 2.68 | 7.87 | 33.0 | .98 | 160. |
| 51-A | 2.2 | 54.8 | 1.6 | .816 | 17.7 | 5.90 | .4 | 181. |
| 49-A | 14.5 | 14.7 | 13.9 | 2.47 | 9.07 | 3.40 | 4.54 | 199. |
| 49 | 3.5 | 30.4 | 3.2 | 0.713 | 18.9 | 5.48 | 0.50 | 246. |
| 6-19-II-B-4 | 8.0 | 15.9 | 5.9. | 0.71 | 22.8 | 29.6 | 0.7 | 337. |
| 6-18-II-M-1A | 19.9 | 129. | 2.0 | 2.60 | 9.95 | 5.4 | 7.0 | 259. |
| 6-18-II-0-1 | 13.5 | 105. | 2.1 | .25 | 14.3 | 14.3 | 4.8 | 606. |
| 43-A | 6.91 | 42.5 | 3.9 | 0.30 | 79.0 | 11.8 | 1.2 | 475. |
| 6-5-III-F ? | 18.6 | 95.4 | 1.8 | .12 | 2.4 | 13.2 | 0.54 | 75.4 |
| 32-B | 3.7 | 68.6 | 2.2 | .15 | 2.7 | 6.96 | 1.29 | 460. |
| 5-29-IV-D | 10.8 | 48.5 | 1.5 | .10 | 1.3 | 1.8 | 0.79 | 43.5 |
| 2/I (21I)? | 14.9 | 68.1 | .82 | .24 | 3.85 | 33.4 | 3.03 | 1560. |
| 54-A | 24.3 | 69.0 | 27.7 | .37 | 389. | 3.4 | 7.0 | 607. |
| 32-A | 3.5 | 137. | 1.4 | .28 | 3.5 | 3.5 | 9.63 | 2070. |

| BLM Sample No. | GSRI Sample No. | BLM Data Sheet for Trace Metal Concentration in 10 ml. Acid Extracts of Benthic Invertebrates | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Ba | V | Cd | Pb | Ni | Cu | Cr | Fe |
| 62-E | BI-1 | 460 | 2,430 | 39 | 29.5 | 690 | 100 | 217 | 27,000 |
| 62-B | BI-2 | 260 | 2,320 | 790 | 63.0 | 24,800 | 160 | 227 | 56,800 |
| 62-A-1 | BI-3 | 430 | 1,580 | 345 | 55.0 | 1,000 | 170 | 119 | 16,900 |
| 60-B | BI-4 | 110 | 2,150 | 5 | 9.0 | 800 | 270 | 8 | 2,782 |
| 60-A | BI-5 | 150 | 2,670 | 670 | 17.0 | 6,200 | 180 | 50 | 12,220 |
| 6-18-II-K-1 | BI-6 | 430 | 2,240 | 16 | 26.8 | 110 | 50 | 128 | 19,800 |
| 51-F | BI-7 | 150 | 1,830 | 190 | 54.5 | 160 | 670 | 20 | 3,250 |
| 51-A | BI-8 | 40 | 1,020 | 30 | 15.2 | 330 | 110 | 8 | 3,380 |
| 49-A | BI-9 | 510 | 520 | 490 | 87.0 | 320 | 120 | 160 | 7,020 |
| 49 | BI-10 | 70 | 610 | 56 | 14.3 | 380 | 110 | 10 | 4,940 |
| 6-19-II-B-4 | BI-11 | 70 | 140 | 52 | 6.2 | 200 | 260 | 6 | 2,960 |
| 6-18-II-M-1A | BI-12 | 260 | 1,690 | 26 | 34.0 | 130 | 70 | 92 | 3,380 |
| 6-18-II-0-1 | BI-13 | 150 | 1,170 | 23 | 2.8 | 160 | 160 | 53 | 6,760 |
| 43-A | BI-14 | 140 | 860 | 79 | 6.0 | 1,600 | 240 | 24 | 9,620 |
| 6-5-III-F | BI-15 | 380 | 1,950 | 37 | 2.5 | 50 | 270 | 11 | 1,540 |
| 32-B | BI-16 | 70 | 1,280 | 42 | 2.8 | 50 | 130 | 24 | 8,580 |
| 5-29-IV-D | BI-17 | 410 | 1,840 | 58 | 3.9 | 50 | 70 | 30 | 1,650 |
| 21I | BI-19 | 580 | 2,650 | 32 | 9.2 | 150 | 1,300 | 118 | 60,690 |
| 54-A | BI-20 | 500 | 1,420 | 570 | 7.7 | 8,000 | 70 | 144 | 12,480 |
| 32-A | BI-21 | 70 | 2,740 | 28 | 5.5 | 70 | 70 | 192 | 41,310 |

APPENDIX D 1

| BLM Sample No. | GSRI Sample No. | BLM Data Sheet for Trace Metal Concentration in 10 ml. Acid Extracts of Zooplankton | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Ba | V | Cd | Pb | Ni | Cu | Cr | Fe |
| ZP-1 | ZP-1-1 | 330 | 22.1 | 41 | 6.5 | 180 | 160 | 11.6 | 1,535 |
| ZP-2 | ZP-2-2 | 70 | 18.5 | 7 | 10.6 | 230 | 130 | 20.2 | 415 |
| ZP-3 | ZP-3-3 | 290 | 13.5 | 105 | 5.8 | 130 | 180 | 8.1 | 420 |
| ZP-9 | ZP-9-4 | 540 | 42.5 | 350 | 11.9 | 170 | 420 | 54 | 3,080 |
| ZP-10 | ZP-10-5 | 1,180 | 58.5 | 45 | 10.3 | 200 | 240 | 28 | 12,245 |
| ZP-11 | ZP-11-6 | 950 | 36.0 | 68 | 7.0 | 127 | 200 | 10.1 | 1,700 |
| ZP-12 | ZP-12-7 | 870 | 69.5 | 46 | 10.4 | 251 | 220 | 26 | 4,895 |
| ZP-13 | ZP-13-8 | 250 | 44.5 | 37 | 8.9 | 200 | 190 | 18.5 | 5,005 |
| ZP-14 | ZP-14-9 | 250 | 55.5 | 39 | 10.7 | 170 | 230 | 6.4 | 960 |
| ZP-15 | ZP-15-10 | 100 | 48.0 | 65 | 4.2 | 237 | 130 | 8.9 | 1,500 |
| ZP-16 | ZP-16-11 | 1,490 | 126.5 | 170 | 11.2 | 320 | 610 | 89 | 21,800 |
| ZP-22 | ZP-22-12 | 630 | 24.5 | 80 | 4.2 | 100 | 160 | 12.2 | 2,760 |
| ZP-23 | ZP-23-13 | 1,180 | 51.5 | 98 | 4.2 | 179 | 200 | 9.5 | 1,860 |
| ZP-24 | ZP-24-14 | 770 | 57.5 | 56 | 10.9 | 50 | 170 | 8.4 | 1,980 |
| ZP-25 | ZP-25-15 | 210 | 50.5 | 107 | 3.6 | 120 | 120 | 7.5 | 1,920 |

APPENDIX E

E.  SAMPLE LOG SUMMARY

    1.  Sediment

    2.  Seawater

        a.  Dissolved Metals
        b.  Suspended Metals

    3.  Aquatic Organisms

        a.  Benthic Invertebrates

        b.  Zooplankton

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APPENDIX E

SAMPLE LOG SUMMARY

APPENDIX E

1.  Sediment

Thirty-five (35) sediment samples (10 grams) were analyzed for
trace metal content for quality control purposes.  The sediments
were assigned a code number by GSRI consisting of the BLM
identification and a number from 1 to 35 to facilitate proper
ordering of samples during laboratory analysis.

The sediment samples analyzed are:

| BLM I.D. | GSRI I.D. |
|:--------:|:---------:|
| 1 | 1-1 |
| 2 | 2-2 |
| 3 | 3-3 |
| 5 | 5-4 |
| 6 | 6-5 |
| 7 | 7-6 |
| 9 | 9-7 |
| 11 | 11-8 |
| 13 | 13-9 |
| 16 | 16-10 |
| 19 | 19-11 |
| 22 | 22-12 |
| 24 | 24-13 |

| BLM I.D. | GSRI I.D. |
|----------|-----------|
| 25 | 25-14 |
| 26 | 26-15 |
| 27 | 27-16 |
| 28 | 28-17 |
| 29 | 29-18 |
| 30 | 30-19 |
| 32 | 32-20 |
| 33 | 33-21 |
| 34 | 34-22 |
| 36 | 36-23 |
| 38 | 38-24 |
| 39 | 39-25 |
| 41 | 41-26 |
| 42 | 42-27 |
| 44 | 44-28 |
| 48 | 48-29 |
| 49 | 49-30 |
| 54 | 54-31 |
| 56 | 56-32 |
| 57 | 57-33 |
| 60 | 60-34 |
| 63 | 63-35 |

2. Seawater

    a.  Dissolved Metals

    Fifteen (15) seawater samples (400 ml) were analyzed for trace
metal content for quality control purposes.  The seawaters were
assigned a code number by GSRI consisting of the BLM identification
and a number from 1 to 15 to facilitate proper ordering of samples
during laboratory analysis.

    The seawater samples analyzed are:

| BLM I.D. | GSRI I.D. |
|----------|-----------|
| TM-363   | TM-363-1  |
| TM-366   | TM-366-2  |
| TM-527   | TM-527-3  |
| TM-530   | TM-530-4  |
| TM-535   | TM-535-5  |
| TM-880   | TM-880-6  |
| TM-889   | TM-889-7  |
| TM-891   | TM-891-8  |
| TM-909   | TM-909-9  |
| TM-917   | TM-917-10 |
| TM-920   | TM-920-11 |
| TM-921   | TM-921-12 |
| TM-922   | TM-922-13 |
| TM-924   | TM-924-14 |
| TM-925   | TM-925-15 |

b. Suspended Metals

Fifteen (15) suspended particulate matter samples (10 ml-extracts)
were analyzed for trace metal content for quality control purposes.
The samples were assigned a code number by GSRI consisting of the BLM
identification and a number from 1 to 15 to facilitate proper ordering
of samples during laboratory analysis.

The suspended particulate matter samples analyzed are:

| BLM I.D. | GSRI I.D. |
|----------|-----------|
| PAD-7 | PAD-7-1 |
| PAD-11 | PAD-11-2 |
| PAD-13 | PAD-13-3 |
| PAD-14 | PAD-14-4 |
| PAD-25 | PAD-25-5 |
| PAD-36 | PAD-36-6 |
| PAD-45 | PAD-45-7 |
| PAD-61 | PAD-61-8 |
| PAD-66 | PAD-66-9 |
| PAD-67 | PAD-67-10 |
| PAD-76 | PAD-76-11 |
| PAD-77 | PAD-77-12 |
| PAD-84 | PAD-84-13 |
| PAD-85 | PAD-85-14 |
| PAD-87 | PAD-87-15 |

3. Aquatic Organisms

   a.  Benthic Invertebrates

   Twenty (20) benthic invertebrate samples (10 ml-extracts) were

analyzed for trace metal content for quality control purposes.

The samples were assigned a code number with prefix "B.I."

(Benthic Invertebrate) and a number from 1 to 21 (sample B.I.-18

was dropped from the Quality Control program by BLM).  The BLM

identification code was considered to be too complex for distribution

in order to maintain proper ordering of samples during laboratory

analysis.

   The benthic invertebrate samples analyzed are:

| BLM I.D. | GSRI I.D. |
|----------|-----------|
| 62-E | B.I.-1 |
| 62-B | B.I.-2 |
| 62-A-1 | B.I.-3 |
| 60-B | B.I.-4 |
| 60-A | B.I.-5 |
| 6-18-II-K-1 | B.I.-6 |
| 51-F | B.I.-7 |
| 51-A | B.I.-8 |
| 49-A | B.I.-9 |
| 49 | B.I.-10 |
| 6-19-II-B-4 | B.I.-11 |
| 6-18-II-M-1A | B.I.-12 |

| BLM I.D. | GSRI I.D. |
|---|---|
| 6-18-II-0-1 | B.I.-13 |
| 43 | B.I.-14 |
| 6-5-III-F | B.I.-15 |
| 32-B | B.I.-16 |
| 5-29-IV-D | B.I.-17 |
| 21-I | B.I.-19 |
| 54-A | B.I.-20 |
| 32-A | B.I.-21 |

b. Zooplankton

Fifteen (15) zooplankton samples (10 ml-extracts) were analyzed for trace metal content for quality control purposes. The zooplankton samples were assigned a code number by GSRI consisting of the BLM identification and a number from 1 to 15 to facilitate proper ordering of samples during laboratory analysis.

The zooplankton samples analyzed are:

| BLM I.D. | GSRI I.D. |
|----------|-----------|
| ZP-1 | ZP-1-1 |
| ZP-2 | ZP-2-2 |
| ZP-3 | ZP-3-3 |
| ZP-9 | ZP-9-4 |
| ZP-10 | ZP-10-5 |
| ZP-11 | ZP-11-6 |
| ZP-12 | ZP-12-7 |
| ZP-13 | ZP-13-8 |
| ZP-14 | ZP-14-9 |
| ZP-15 | ZP-15-10 |
| ZP-16 | ZP-16-11 |
| ZP-22 | ZP-22-12 |
| ZP-23 | ZP-23-13 |
| ZP-24 | ZP-24-14 |
| ZP-25 | ZP-25-15 |

**The Department of the Interior Mission**

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources.  This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

**The Minerals Management Service Mission**

As a bureau of the Department of the Interior, the Minerals Management Service's (MMS) primary responsibilities are to manage the mineral resources located on the Nation's Outer Continental Shelf (OCS), collect revenue from the Federal OCS and onshore Federal and Indian lands, and distribute those revenues.

Moreover, in working to meet its responsibilities, the **Offshore Minerals Management Program** administers the OCS competitive leasing program and oversees the safe and environmentally sound exploration and production of our Nation's offshore natural gas, oil and other mineral resources.  The MMS **Minerals Revenue Management** meets its responsibilities by ensuring the efficient, timely and accurate collection and disbursement of revenue from mineral leasing and production due to Indian tribes and allottees, States and the U.S. Treasury.

The MMS strives to fulfill its responsibilities through the general guiding principles of:  (1) being responsive to the public's concerns and interests by maintaining a dialogue with all potentially affected parties and (2) carrying out its programs with an emphasis on working to enhance the quality of life for all Americans by lending MMS assistance and expertise to economic development and environmental protection.