# METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY— IN-BOTTLE ACID DIGESTION OF WHOLE-WATER SAMPLES

## By Gerald L. Hoffman, Marvin J. Fishman, and John R. Garbarino

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# CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

| Multiply | By | To obtain |
|---|---|---|
| gram (g) | $3.52 \times 10^{-2}$ | ounce, avoirdupois |
| microgram (µg) | $3.52 \times 10^{-8}$ | ounce |
| liter (L) | $2.64 \times 10^{-1}$ | gallon |
| milliliter (mL) | $2.64 \times 10^{-4}$ | gallon |

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5 \ (°C) + 32.$$

**The following water-quality terms also are used in this report:**

| | |
|---|---|
| µg/g | microgram per gram |
| µg/L | microgram per liter |

**Other abbreviations are as follows:**

| | |
|---|---|
| AAS | atomic absorption spectrophotometry |
| ASTM | American Society for Testing and Materials |
| MIB | modified in-bottle procedure |
| $N$ | normality (equivalents per liter) |
| NIST | National Institute of Standards and Technology |
| NWQL | National Water Quality Laboratory |
| OIB | original in-bottle procedure |
| SRM | standard reference material |
| sp. gr. | specific gravity |
| USGS | U.S. Geological Survey |
| v/v | volume per volume |

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## Abstract

Water samples for trace-metal determinations routinely have been prepared in open laboratories. For example, the U.S. Geological Survey method I-3485-85 (Extraction Procedure, for Water-Suspended Sediment) is performed in a laboratory hood on a laboratory bench without any special precautions to control airborne contamination. This method tends to be contamination prone for several trace metals primarily because the samples are transferred, acidified, digested, and filtered in an open laboratory environment. To reduce trace-metal contamination of digested water samples, procedures were established that rely on minimizing sample-transfer steps and using a class-100 clean bench during sample filtration. This new procedure involves the following steps:

1. The sample is acidified with HCl directly in the original water-sample bottle.

2. The water-sample bottle with the cap secured is heated in a laboratory oven.

3. The digestate is filtered in a class-100 laminar-flow clean bench.

The exact conditions used (that is, oven temperature, time of heating, and filtration methods) for this digestion procedure are described. Comparisons between the previous U.S. Geological Survey open-beaker method I-3485-85 and the new in-bottle procedure for synthetic and field-collected water samples are given. When the new procedure is used, blank concentrations for most trace metals determined are reduced significantly.

## INTRODUCTION

The U.S. Geological Survey (USGS) since 1972 has been using an acid-digestion procedure as preliminary treatment of whole-water samples (water-suspended sediment) to desorb and solubilize trace metals associated with the suspended-sediment phase of the sample. Normally, less than 95 percent of the metals are solubilized by this technique, and the results are reported as "whole water recoverable" (Fishman and Friedman, 1989). In this procedure, the samples were digested by heating with dilute hydrochloric acid in an open beaker on a hot plate. The samples were heated to just below boiling in a laboratory hood and heating continued until the volume was reduced approximately 20 percent. Following digestion, the samples were filtered to remove particulate matter, diluted to the original volume with water, and aliquots of the filtrates were analyzed for metals by appropriate methods. This procedure tends to be contamination prone for several trace metals primarily because the samples are transferred, acidified, digested, and filtered in an open laboratory environment.

To avoid this contamination problem, a new acid-digestion procedure was developed, which minimizes sample transfer steps and requires filtration in a class-100 clean bench. The procedure involves acid digestion of whole-water samples in capped polyethylene bottles at 65°C for 8 hours and filtration in class-100 clean room conditions. The new acid-digestion in-bottle method was developed to achieve equivalent extraction efficiency with the open-beaker method. The method was developed by the USGS for use in the Survey's National Water Quality Laboratory (NWQL).

The in-bottle method was implemented at the NWQL in April 1992. A detailed description of all aspects of the method from application through reporting of results is provided. Precision, accuracy, and comparability data to the former method are presented for trace metals using appropriate procedures. The precision and accuracy of trace metal concentrations solubilized using the in-bottle method are compared to the open-beaker method.

## ANALYTICAL METHOD

## Metals, extraction procedure, acid digestion, whole water recoverable, I-3486-95

### 1. Application

This in-bottle method is used as preliminary treatment of whole-water samples to desorb and solubilize trace metals associated with the suspended-sediment phase of the sample. If greater than 95 percent of the substance to be determined is solubilized, the results should be reported as "total." If less than 95 percent is solubilized or the percent solubilized is not known, the results should be reported as "whole water recoverable."

### 2. Summary of method

2.1 The sample is digested by oven heating with dilute hydrochloric acid in the original sample bottle. Following digestion, the sample is filtered inside a class-100 clean bench to remove particulate matter, and aliquots of the filtrate are analyzed for metals by atomic absorption spectrophotometry (AAS) or other approved methods.

2.2 For additional information on principles of the methods, see individual methods for each trace metal (Fishman and Friedman, 1989; Fishman, 1993).

### 3. Interferences

There are no interferences in the acid-digestion procedure.

### 4. Apparatus and materials

4.1 *Clean bench*, class-100.

4.2 *Filter paper*, Whatman No. 41 or equivalent.

4.3 *Filter funnels*, disposable, Whatman No. 1920-1441 or equivalent.

4.4 *Drying oven*; mechanical convection heating, with a time and temperature controller accurate to ±1 percent.

4.5 *Analytical balance*, Mettler Model PM600; 0 to 600-g range; capable of accurately weighing to 0.01 g; VWR Scientific; Model 11275-260 or equivalent.

4.6 *Sample bottles*, polypropylene or polyethylene capable of being heated to 85°C without deforming.

4.7 *Filter funnel racks, adjustable*; made from polypropylene or any suitable plastic not effected by dilute acid.

### 5. Reagents

5.1 *Hydrochloric acid,* concentrated (sp. gr. 1.19), Baker Instra-analyzed or equivalent.

5.2 *Nitric acid, 0.1 N.* Add 6.4 mL concentrated $HNO_3$ (sp. gr. 1.41), Baker Instra-analyzed or equivalent to 400 mL water and dilute to 1 L with water.

5.3 *Water.* All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1995).

# 6. Procedure

The following procedure and conditions for the in-bottle digestion were determined using the results of the temperature and time study described in the Discussion of Results section of this report. A different set of conditions with equivalent results are described in Appendix B.

6.1   Weigh the sample bottle, cap, and sample to determine the gross weight.

6.2   Subtract the average weight of an identical size capped bottle to determine the volume of sample.

6.3   Add 1.25 mL concentrated HCl for each 50 mL of sample.

6.4   Recap the bottle and shake vigorously.

**NOTE 1:** Prepare a blank and a standard reference water sample with each set of samples to be digested. Add an equivalent amount of HCl to each.

6.5   Place the recapped samples, blank, and reference samples in a 65°C oven. Maintain the samples at this oven temperature setting for 8 hours. Do not correct the 8-hour heating time for the time required for the samples to reach 65°C.

6.6   Filtration apparatus preparation

6.6.1   Open the sealed disposable-filter funnels containing filters in a class-100 clean bench and place in filter-funnel racks.

6.6.2   Fill each filter funnel rapidly with 250 mL of 0.1 $N$ HNO$_3$ and repeat with an additional 250 mL of 0.1 $N$ HNO$_3$.

6.6.3   Fill each funnel rapidly three times using 250 mL of water for each rinse. Allow the funnels to drain completely between rinses.

6.7   Sample filtration

6.7.1   Place an empty acid-rinsed labeled bottle under each filter funnel.

6.7.2   Shake each sample after removal from oven, let stand 30 minutes, and pour the contents of each digested sample through the filter funnels.

**NOTE 2:** Filtration of 100 percent of the sample volume is not required if the bottles are shaken vigorously after removal from oven. At least 75 percent of the sample volume should be filtered to ensure sufficient sample for the required analysis.

**NOTE 3:** If a filter becomes plugged with sediment during filtration, replace it with a clean filter funnel.

6.7.3   Rinse sample bottles twice with water. Dispose of wash solution in a suitable container clearly labeled as acid waste.

6.7.4   Transfer filtered samples to original sample bottles. Close using the caps from the filtrate bottles.

**NOTE 4:** The original sample bottles have a large amount of information written on them. It is easier to transfer the sample back to the original bottle than to transcribe all the information to the new sample bottle.

6.7.5   Use aliquots of these filtered solutions to determine acid-soluble metals as required by appropriate methods.

# 7. Calculations

The methods used to determine the metal concentrations by AAS are given by Fishman and Friedman (1989) and Fishman (1993).

## 8. Reporting of results

The significant figures to be reported are given by Fishman and Friedman (1989) and Fishman (1993).

## 9. Precision

See section on Precision under Discussion of Results.

## DISCUSSION OF RESULTS

### Synthetic Whole-Water Samples

Two synthetic whole-water samples were used in this study to determine the in-bottle method conditions necessary to approximate the digestion yields obtainable with the open-beaker method. Synthetic whole-water samples were used primarily because they could be duplicated at a later time if needed. For example, a new set of synthetic whole-water samples was made several months after the initial temperature and time study was completed to test the precision of the in-bottle method.

The two synthetic whole-water samples containing particulate matter were made by adding appropriate amounts of two different National Institute of Standards and Technology (NIST) reference sediments to 200 mL of 0.1 $N$ nitric acid. The two standard reference materials (SRM) used were river sediment SRM 1645 (0.1 g) and estuarine sediment SRM 1646 (0.3 g). After addition of the standard reference material, the synthetic whole-water samples were shaken and allowed to stand at room temperature for 3 days to simulate real whole-water samples collected and acidified in the field. The synthetic whole-water samples were subsequently digested by USGS Procedure I-3485 (Fishman and Friedman, 1989) open-beaker method or by the in-bottle method.

To calculate percent recovery for metals in the synthetic whole-water samples for the in-bottle and open-beaker methods used in this study, the following equations were used:

$$T = C \times V \qquad (1)$$

where $T$ = weight of metal determined in the synthetic water digestate, in micrograms;

$C$ = measured metal concentration in synthetic water digestate, in micrograms per liter; and

$V$ = volume of synthetic water digestate, in liters.

$$M = T_{NIST} \times W \qquad (2)$$

where $M$ = certified metal content of the weighed sediment added to the synthetic water sample, in micrograms;

$T_{NIST}$ = metal concentration in the NIST standard, in micrograms per gram; and

$W$ = weight of the NIST standard used in preparing synthetic water samples, in grams.

$$\text{Percent recovery} = \frac{T}{M} \times 100 \qquad (3)$$

### Comparison Studies between In-Bottle and Open-Beaker Methods

#### Temperature and Time

Two conditions that affect the solubilization of trace metals from waterborne particulate matter by the in-bottle and open-beaker methods are the temperature of the sample and time of

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digestion, assuming that the quantity of acid used in dissolution is identical for both methods. The primary objective of a temperature and time of heating study for the in-bottle method was to determine if any metals measured in the synthetic whole-water samples were released from the particulate matter in a predictable fashion. For example, if a given metal is solubilized at 65°C as a linear function of time, then the resulting metal concentration can be used to establish the time required for heating samples to give comparable results to the open-beaker method. Any metal that is totally solubilized or does not show any increase with time of heating cannot be used to establish the heating time for the in-bottle method compared to the open-beaker method.

To determine the appropriate heating conditions for the in-bottle method, the following study was conducted. A total of 24 synthetic whole-water samples was acidified with concentrated HCl (1.25 mL per 50 mL of sample) and heated in a conventional laboratory oven maintained at 65°C. Twelve samples were NIST estuarine-sediment-water samples, and 12 samples were NIST river-sediment-water samples. Three estuarine-sediment and three river-sediment whole-water samples were removed from the oven after 4, 8, 16, and 32 hours. The synthetic whole-water samples were shaken, allowed to cool at ambient temperature for 30 minutes, and then were filtered through plastic funnels using Whatman No. 41 filter paper into acid-cleaned bottles. The samples were filtered in a class-100 clean bench. A duplicate set of six synthetic whole-water samples (three estuarine and three river sediment) was acidified with an equivalent amount of concentrated HCl, heated, filtered, and transferred using the open-beaker method. All samples then were analyzed for trace metals by AAS. Conventional flame atomization was used to determine iron, manganese, and zinc, and graphite furnace atomization was used to determine cadmium, cobalt, copper, lead, and nickel. The entire experiment described above was duplicated at 85°C to

analyze the effect of a temperature increase on yields for the in-bottle method for trace-metal solubilization. The polyethylene bottles deformed above 85°C.

Figures 1 through 16 (see Appendix A) show the percent recovery for eight metals determined in both the estuarine and river sediment synthetic whole-water samples by the in-bottle digestion method. Each figure also shows the mean percent recovery by the open-beaker method. This percent recovery is depicted as an open triangle on figures 1 through 16. The upper and lower boundaries of the standard deviation of the mean percent recovery are indicated as a vertical tick mark. The horizontal dashed lines emanating from the standard deviation tick marks for the open-beaker method aid in establishing the temperature and time required to obtain equivalent recovery by the in-bottle method. A 100-percent recovery concentration was calculated for each metal in the two synthetic whole-water samples and is listed on each figure. These theoretical concentrations were calculated using the NIST certified concentrations for each metal in each sediment sample.

For example, the iron concentrations determined in both synthetic whole-water samples (figs. 7 and 8) were between 10,000 and 40,000 µg/L. These high concentrations effectively minimize the possibility that contamination might produce error in the analytical results. In contrast, the calculated cadmium concentration for the estuarine synthetic whole-water sample (fig. 1) is approximately 0.5 µg/L. There could be contamination and detection-limit problems that would affect the reliability of measured values of cadmium at this concentration. The other metals measured in the synthetic water samples had concentrations that fell between the two extremes of iron (high) and cadmium (low).

Cadmium, lead, and zinc (see figs. 1, 2, 9, 10, and 15 in Appendix A) determined in either of the synthetic samples

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show recoveries greater than 80 percent at the minimum heating time of 4 hours. These data could not be used to determine the temperature and time requirements for the in-bottle method because there was little or no change in the percentage recovery with increased heating or increased time of digestion. Other metals determined (cobalt, copper, manganese, and nickel) show increases in percent recovery with increases in time of digestion. However, the increases in percent recovery are not as pronounced as the results for iron.

Iron was the best metal used to determine the time and heating conditions for the in-bottle method. There was a definite increase in the iron concentration with the increase of time of heating for both samples (figs. 7 and 8). Also, there was an increase in the iron concentration at 85°C compared to 65°C at each time interval. Cadmium, lead, and zinc showed no significant difference in concentration for samples heated at 65° or 85°C, suggesting that these metals are adsorbed on the surface of the sediments, are not part of the internal structure, and are easily solubilized. However, for iron, results suggest that the digestion procedure was slowly breaking down the particulate structure of the sediment. The iron concentrations determined by the in-bottle method indicate that a temperature of 65°C and a heating time of 8 hours approximate the iron data for the open-beaker method.

## Precision

The precision of the in-bottle and open-beaker methods is dependent on reproducibility of the digestion, homogeneity of the samples, and metal contamination incurred during the digestion. The analytical methods (AAS–flame atomization and AAS–graphite furnace atomization) were the same for both in-bottle and open-beaker methods, and, therefore, should not influence the selection of one digestion method over the other. All samples used to determine

precision were matched (synthetic whole water) or were homogenized (natural-water samples) before being split. Only two variables were of concern: (1) the contamination potential, and (2) the ability to reproduce the exact temperature and time of heating).

The potential for contamination of the open-beaker method was not altered for this precision study (for example, ultraclean conditions were not used). The contamination variable in part accounts for a decrease in precision for the open-beaker method compared to the in-bottle procedure.

The ability to reproduce the exact heating conditions for the open-beaker method is questionable because the procedure is not specific enough to ensure reproducibility. For example, the open-beaker method states, "Heat solution in beaker to just below boiling and continue heating until the volume is reduced approximately 20 percent" (Fishman and Friedman, 1989, p. 50). The term "just below boiling" is not specified and may vary from day to day depending on the analyst. The second term concerning the reduction in volume as it relates to time of heating is not reproducible because it requires a subjective measurement as to volume changes.

For the purposes of this study, these terms were used as follows: (1) just below boiling was defined as 90°C ±5°C, and (2) reduction in volume was defined to mean 20 percent ±5 percent. To ensure a solution temperature of 90°C on the hot plate, a beaker filled with deionized water was placed on the hot plate and monitored for temperature with a mercury thermometer. When the temperature of the water had stabilized for one-half hour, the synthetic water samples were placed on the hot plate for digestion. To ensure that the correct volume of water had evaporated, the beakers were marked with two volume lines. The first line indicated total volume (200 mL), and the second line represented a volume reduction of 20 percent (160 mL). With these prescribed

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conditions, approximately 30 minutes were required to reduce the volume 20 percent. These exact conditions of the open-beaker method were used only for experiments to establish the temperature and time of heating requirements for the in-bottle method. All of the results for samples digested by the in-bottle and open-beaker methods are referenced to this set of conditions in which the temperature and time of heating for the open-beaker method were rigidly controlled.

Three different types of whole-water samples were digested to test the in-bottle and open-beaker methods for precision and possible contamination. It was necessary to determine the precision of the open-beaker method because no previous precision data existed. This study was conducted for a 3-week period. On one day of each of three consecutive weeks, the following sets of identical samples were digested by both procedures: (1) three blank-water samples, (2) three synthetic NIST estuarine whole-water samples, and (3) three synthetic NIST river whole-water samples—a total of nine blank, nine estuarine, and nine river whole-water synthetic samples.

In addition, each week for 3 weeks, 10 natural whole-water samples were selected at random from samples logged into the laboratory. These samples were homogenized by shaking vigorously for 5 minutes and then were split into two equal portions in acid-cleaned bottles. Each set of samples was processed by the in-bottle and open-beaker methods at the same time that the blank and synthetic samples were processed.

All the samples processed by the open-beaker method were handled in a routine manner and were included as part of a normal set of whole-water samples processed on that day. The temperature of the hot plate and time of heating were not controlled rigorously as was the case for the temperature and time of heating experiment used to establish the in-bottle digestion conditions. These samples were processed without rigorous temperature and time of heating conditions to estimate the precision of the open-beaker digestion method as routinely used, and to determine if a lack of control would change the trace-metal recoveries compared to the rigorously controlled open-beaker method. Results of the precision studies follow.

## Blank-Concentration Data

Blank samples (0.1 $N$ HNO$_3$) were analyzed in triplicate over a 3-week period for a total of nine replicates using the in-bottle and open-beaker methods. On the basis of the earlier study of time and temperature, the digestion conditions for the in-bottle method were 8 hours at 65°C. All of the digested blanks from both methods then were analyzed for trace metals by AAS–graphite furnace atomization. The results from this study are listed in table 1. For all eight trace metals, the concentrations measured by the in-bottle method are less than those measured by the open-beaker method. Concentrations measured for cadmium, cobalt, copper, iron, lead, nickel, and zinc for the in-bottle digestion method were less than the detection limit of the analytical methods. Manganese was the only exception; the concentration measured for the in-bottle method was four times less than the concentration measured for the open-beaker method. Thus, the study shows there is less contamination by in-bottle digestion.

## Synthetic Whole-Water Sample Data

All trace metals were determined by AAS using either flame atomization or graphite furnace atomization, depending on the sensitivity required. The precision for the in-bottle and open-beaker methods was determined using the F-test ($\alpha=0.05$) for the comparison of standard deviations. Each of the two sets (NIST estuarine or river) of synthetic whole-water samples was analyzed for eight trace metals

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**Table 1.** Contamination of blank samples by the in-bottle and open-beaker methods

[All concentrations in micrograms per liter. <, less than; —, data not available]

| Trace metal | In-bottle method | | Open-beaker method | |
|---|---|---|---|---|
| | Mean | Standard deviation | Mean | Standard deviation |
| Cadmium | <0.05 | — | 0.13 | 0.05 |
| Cobalt | < .5 | — | .7 | .3 |
| Copper | < .5 | — | 1.8 | .7 |
| Iron | <1 | — | 18.3 | 5.5 |
| Lead | < .5 | — | 2.9 | 1.8 |
| Manganese | .28 | 0.20 | 1.2 | .8 |
| Nickel | < .5 | — | 3.0 | 1.5 |
| Zinc | <1 | — | 10.0 | 4.2 |

(cadmium, cobalt, copper, iron, lead, manganese, nickel, and zinc); therefore, 16 data sets consisting of 9 replicates each were tested. Of the 16 data sets, 8 metals indicate no significant difference in precision for the samples digested by the in-bottle method or the open-beaker method. Of the remaining eight data sets, six metals indicate that the in-bottle method is more precise than the open-beaker method.

For most trace metals (table 2), the mean concentrations are slightly greater with the open-beaker method. The tendency of the open-beaker method to give higher concentrations for the trace metals determined in the estuarine and river synthetic whole-water samples might indicate that the heating conditions routinely applied to the open-beaker method in this 3-week test period were more intense than the heating conditions established for the temperature and time of heating experiment. The digestion conditions for the in-bottle method were 8 hours at 65°C (see table 2). To test this hypothesis, Student $t$-tests were applied to the data to determine if the means from the 3-week tests are equal to the means of the temperature and time of heating tests. Iron is the best example to test because of the response to temperature and time of heating (see figs. 7 and 8 in Appendix A). The Student $t$-test statistic was calculated several ways using the 3-week precision

data and the original data establishing the temperature and time of heating conditions. The following definitions further simplify discussion of the Student $t$-tests:

OBE-1 = open-beaker method, original estuarine whole-water samples;

OBR-1 = open-beaker method, original river whole-water samples;

IBE-1 = in-bottle method, original estuarine whole-water samples;

IBR-1 = in-bottle method, original river whole-water samples;

OBE-2 = open-beaker method, 3-week precision estuarine whole-water samples;

OBR-2 = open-beaker method, 3-week precision river whole-water samples;

IBE-2 = in-bottle method, 3-week precision estuarine whole-water samples; and

IBR-2 = in-bottle method, 3-week precision river whole-water samples.

The iron data used for the IBE-1 and IBR-1 samples corresponded to the 65°C at 8 hours of heating taken from figures 7 and 8 (see Appendix A). These sample data correspond to the conditions required to approximate the percent recovery data produced for iron by the open-beaker method when the digestion conditions were controlled.

**Table 2.** Data on river and estuarine sediment synthetic whole-water samples using in-bottle and open-beaker methods

[All concentrations in micrograms per liter. Std. dev., standard deviation; E, estuarine sample; R, river sample]

| Trace metal | Sample type | Digestion | | | |
|---|---|---|---|---|---|
| | | In-bottle method | | Open-beaker method | |
| | | Mean | Std. dev. | Mean | Std. dev. |
| Cadmium | E | 0.48 | 0.01 | 0.65 | 0.16 |
| Cadmium | R | 4.3 | .4 | 4.2 | .2 |
| Cobalt | E | 8.1 | .6 | 9.6 | .7 |
| Cobalt | R | 2.7 | .5 | 3.0 | .5 |
| Copper | E | 15.2 | .7 | 19.6 | 1.1 |
| Copper | R | 47.6 | 4.9 | 48.2 | 5.8 |
| Iron | E | 29,200 | 1,300 | 34,500 | 2,300 |
| Iron | R | 25,200 | 2,600 | 34,200 | 5,700 |
| Lead | E | 26.7 | .7 | 32.1 | 2.7 |
| Lead | R | 375 | 45 | 352 | 18 |
| Manganese | E | 275 | 15 | 273 | 7 |
| Manganese | R | 280 | 30 | 312 | 32 |
| Nickel | E | 22.4 | .9 | 30 | 2.6 |
| Nickel | R | 16.2 | 2.2 | 19.7 | 2.8 |
| Zinc | E | 156 | 4 | 175 | 9.7 |
| Zinc | R | 889 | 85 | 840 | 33 |

The first condition tested (OBE-2 in relation to OBE-1) shows a significant difference between the means for iron. The second and third conditions tested (IBE-2 in relation to OBE-1 and IBE-2 in relation to IBE-1) show no significant difference between the means for iron. The fourth condition tested (OBE-2 in relation to IBE-2) shows a significant difference between the means for iron.

The same series of Student $t$-tests was applied to the river whole-water synthetic samples for the iron data. The results of the Student $t$-tests were identical to those given for the estuarine whole-water synthetic samples. The conclusions that can be inferred from these statistical tests are as follows: (1) The in-bottle heating conditions can be reproduced from week to week; and (2) the lack of temperature and time of heating controls for the open-beaker method might cause variations in the percent recovery for the metals.

## Natural-Water Sample Data

Ten natural-water samples were selected for comparison each week for 3 weeks for a total of 30 samples. These water samples were thoroughly mixed by manually shaking the bottles for at least 5 minutes. The water then was rapidly poured into two separate acid-cleaned bottles. Each week one set of the split samples was processed by the in-bottle method, and the second set was processed by the open-beaker method. All of the samples were analyzed by one analyst on

one day. The metals were determined by AAS, using either flame atomization or graphite furnace atomization, depending on the sensitivity required for a given determination.

The results of this comparison study are shown in figures 17 through 24 (see Appendix A). The correlation coefficient and the calculated and plotted linear regression line for each metal are shown in these figures. The in-bottle method was chosen as the independent variable because of less error associated with contamination of samples and less variability in results owing to the control of temperature and time of heating. The plotted data tend to confirm that contamination or lack of digestion control were sources of error for the open-beaker method.

For example, the first error source is shown by the large amount of scatter for nickel data in figure 23. Random contamination of samples analyzed for nickel by the open-beaker method would be consistent with this type of result. The calculated intercept for the linear regression line is 2.11 $\mu$g/L. This calculated intercept is approximately that of the mean blank concentration of 3.0 $\mu$g/L for nickel in the open-beaker method listed in table 1. The calculated intercepts for all the other metals determined (except iron) are also consistent with the contamination measured in blanks by the open-beaker method. Blank data listed in table 1 were obtained at the same time that the natural whole-water samples were analyzed. It is reasonable to assume that contamination measured in the open-beaker blanks is probably present in the open-beaker samples. However, it is not realistic to correct the data because the contamination is not constant.

The second error source that can increase or decrease the metal concentration by the open-beaker method is the lack of control of temperature and time of heating for samples. The calculated intercept of the linear regression line for iron cannot be explained by contamina-

tion. The mean iron blank contamination for the open-beaker method is 18.3 $\mu$g/L. The intercept for the plotted iron data (fig. 20) is 326 $\mu$g/L. The previous Student $t$-tests described for the precision studies can be used to explain the excess iron indicated by the intercept (see fig. 20). All of the natural-water samples processed by the open-beaker method were digested at the same time that the synthetic whole-water samples used for the precision studies were digested. The conclusions drawn from the statistical analysis for the synthetic whole-water samples should be applicable to the natural-water samples determined for iron.

The data were tested directly using the matched-pair $t$-test. The $t$-test indicated that there was no significant difference (at $\alpha=0.05$) in cobalt, iron, manganese, and zinc concentrations for sample pairs digested by the two different methods; all the rest of the metal concentrations were significantly different. If blank concentrations are subtracted from respective metal concentrations for the open-beaker method, the $t$-test indicated that there was no significant difference between the two digestion procedures for any of the metals determined. There was no significant change in the calculated $t$-statistic for iron, manganese, and zinc after the blank corrections were made to the unprocessed data, because the blank correction was less than 1 percent of the respective means of these trace metals. However, blank corrections for copper, lead, and nickel significantly changed the $t$-statistic for these metals. The blank corrections were 20 percent (copper), 30 percent (lead), and 50 percent (nickel) of the mean measured concentrations.

## CONCLUSIONS

The in-bottle method gave improved reproducibility and lower blank concentrations for metals in whole-water samples than the previously used open-beaker method (Fishman and Friedman, 1989). Also, the precision studies show the validity of using synthetic whole-water

samples. It should be possible to use this same type of synthetic whole-water sample to test other types of digestion procedures and relate the results back to this study. Such a study has been done and is reported in Appendix B.

## REFERENCES CITED

American Society for Testing and Materials, 1995, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 122–124.

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 217 p.

Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.

# APPENDIX A—GRAPHS SHOWING ACID DIGESTION OF SYNTHETIC WHOLE-WATER SAMPLES AND TRACE-METAL DATA USING IN-BOTTLE AND OPEN-BEAKER METHODS
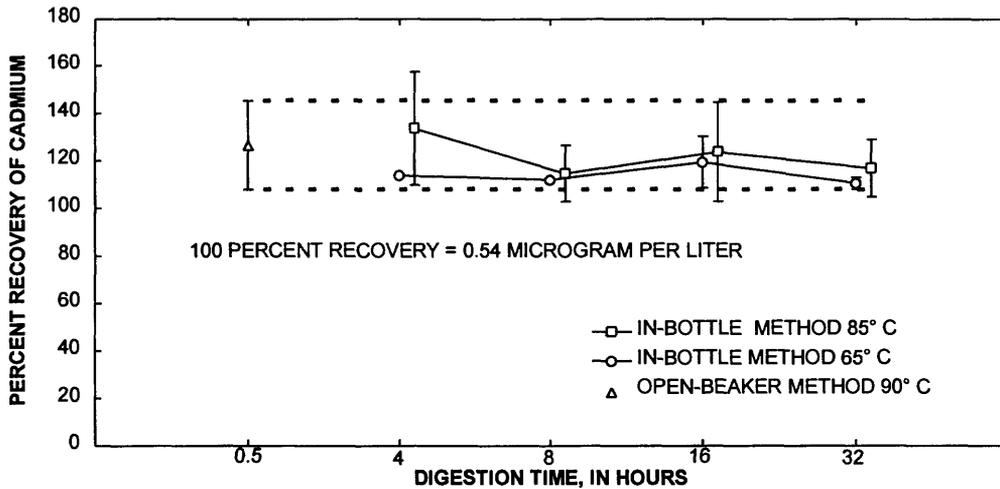
Figure 1. Acid digestion of synthetic whole-water samples made from estuarine sediment to determine time and temperature requirements of the in-bottle method to obtain data equivalent to the open-beaker method for cadmium.
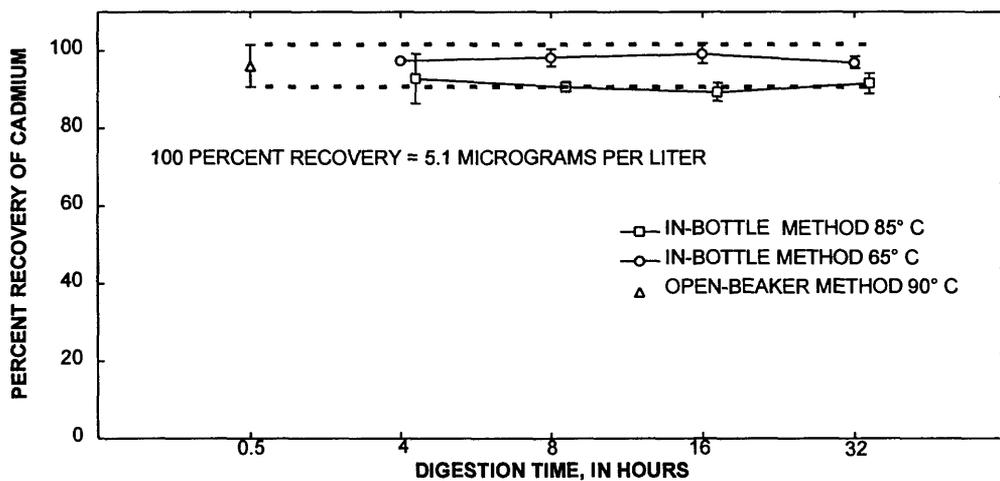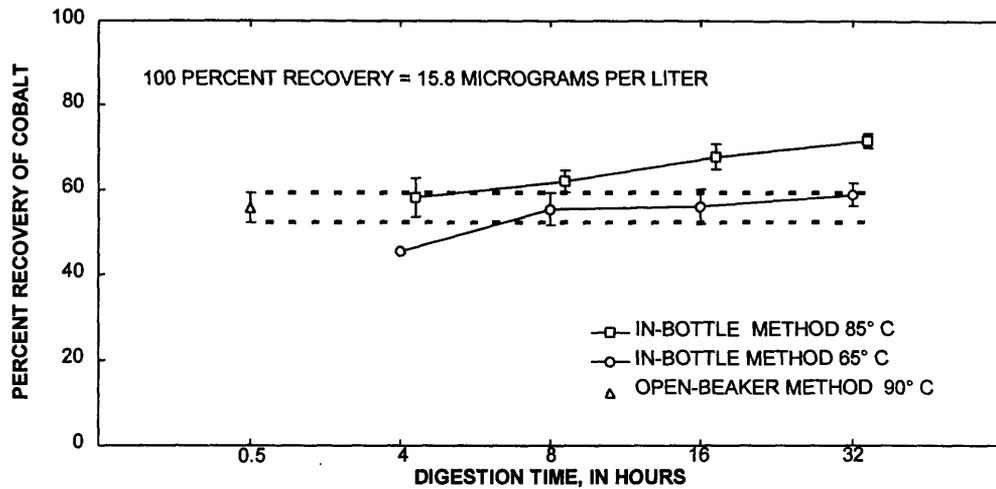(Dashed lines indicate standard deviation for open-beaker method.)
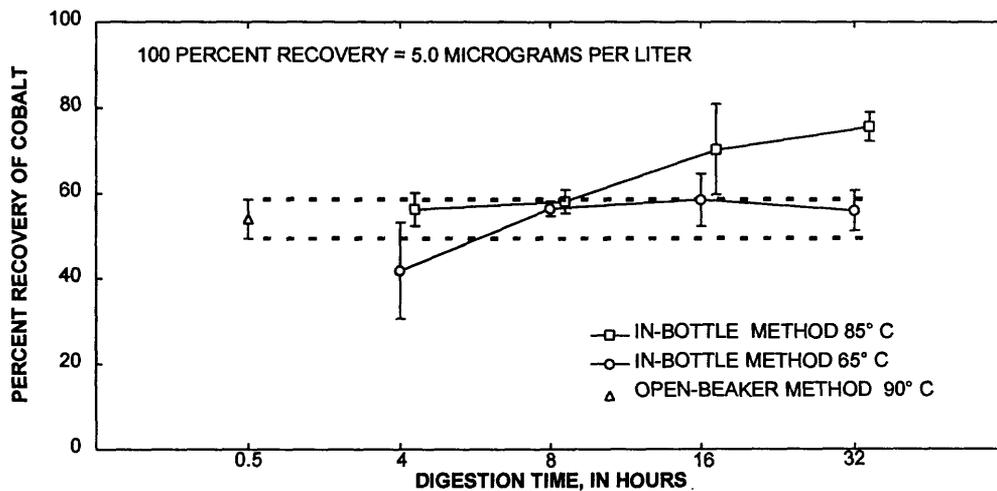


Figure 2. Acid digestion of synthetic whole-water samples made from river sediment to determine time and temperature requirements of the in-bottle method to obtain data equivalent to the open-beaker method for cadmium.
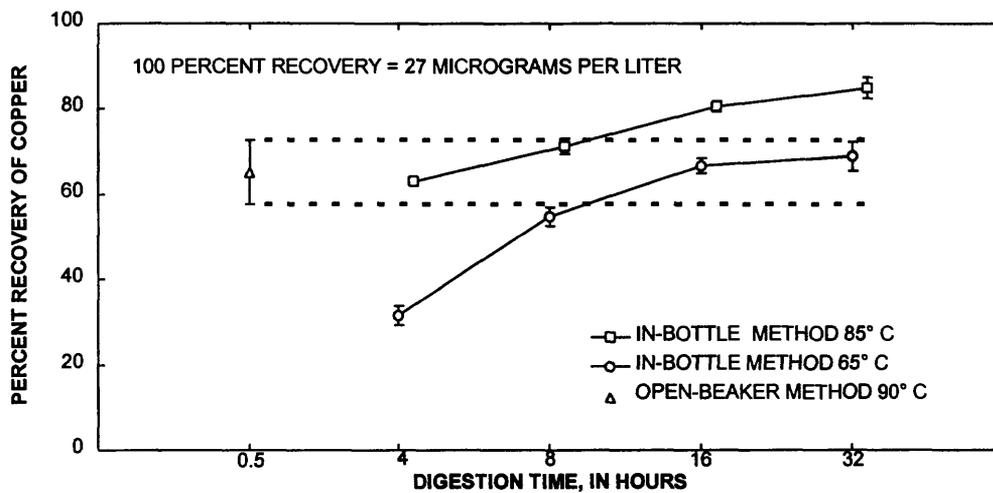(Dashed lines indicate standard deviation for open-beaker method.)

Figure 3. Acid digestion of synthetic whole-water samples made from estuarine sediment
to determine time and temperature requirements of the in-bottle method to
obtain data equivalent to the open-beaker method for cobalt.
(Dashed lines indicate standard deviation for open-beaker method.)
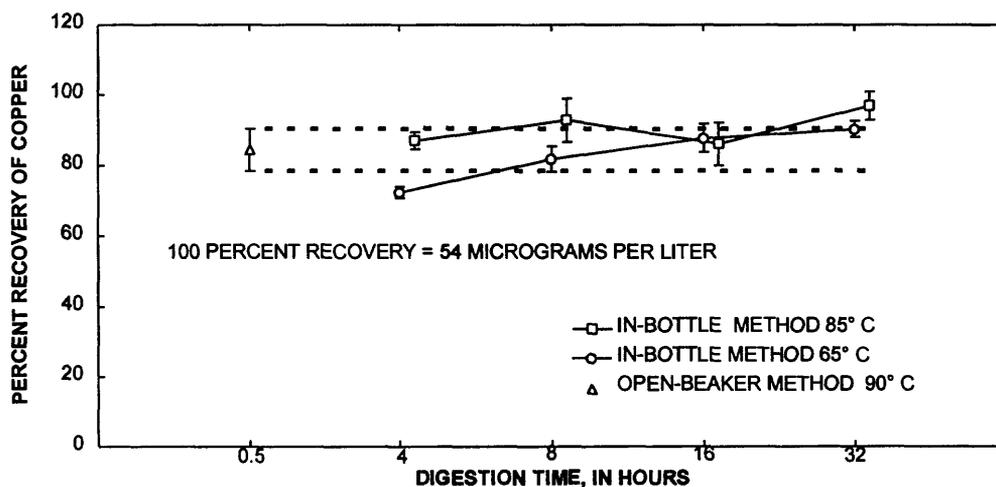


Figure 4. Acid digestion of synthetic whole-water samples made from river sediment
to determine time and temperature requirements of the in-bottle method to
obtain data equivalent to the open-beaker method for cobalt.
(Dashed lines indicate standard deviation for open-beaker method.)

Figure 5. Acid digestion of synthetic whole-water samples made from estuarine sediment to determine time and temperature requirements of the in-bottle method to obtain data equivalent to the open-beaker method for copper.
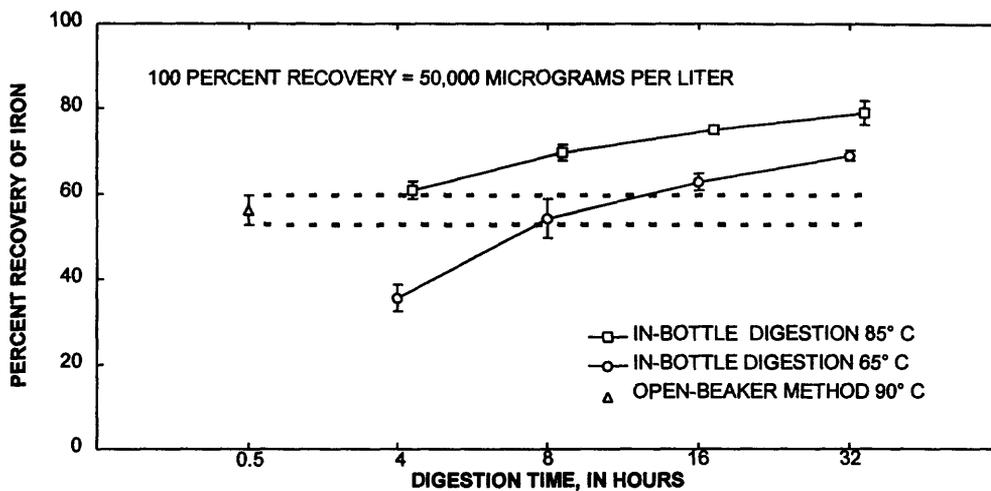(Dashed lines indicate standard deviation for open-beaker method.)



Figure 6. Acid digestion of synthetic whole-water samples made from river sediment to determine time and temperature requirements of the in-bottle method to obtain data equivalent to the open-beaker method for copper.
(Dashed lines indicate standard deviation for open-beaker method.)

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Figure 7. Acid digestion of synthetic whole-water samples made from estuarine sediment
to determine time and temperature requirements of the in-bottle method to
obtain data equivalent to the open-beaker method for iron.
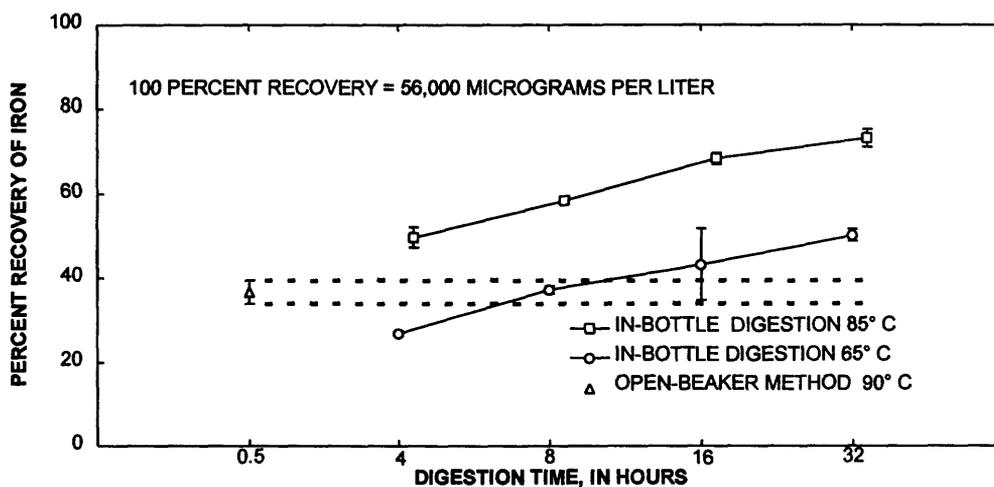(Dashed lines indicate standard deviation for open-beaker method.)



Figure 8. Acid digestion of synthetic whole-water samples made from river sediment
to determine time and temperature requirements of the in-bottle method to
obtain data equivalent to the open-beaker method for iron.
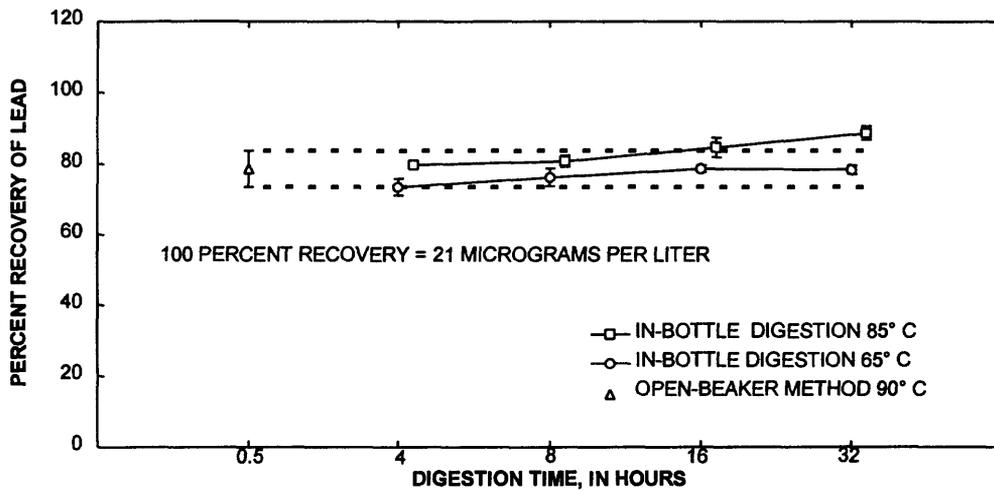(Dashed lines indicate standard deviation for open-beaker method.)

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Figure 9. Acid digestion of synthetic whole-water samples made from estuarine sediment
to determine time and temperature requirements of the in-bottle method to
obtain data equivalent to the open-beaker method for lead.
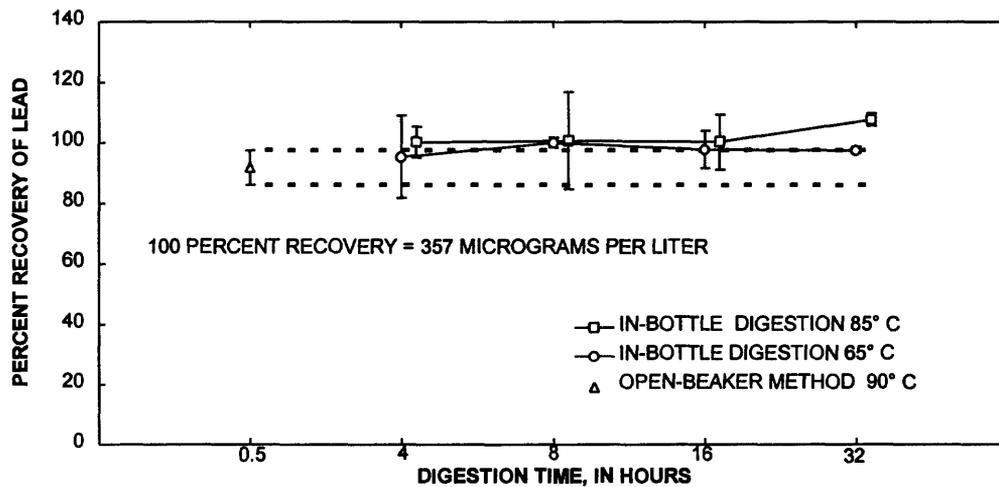(Dashed lines indicate standard deviation for open-beaker method.)



Figure 10. Acid digestion of synthetic whole-water samples made from river
sediment to determine time and temperature requirements of the in-bottle
method to obtain data equivalent to the open-beaker method for lead.
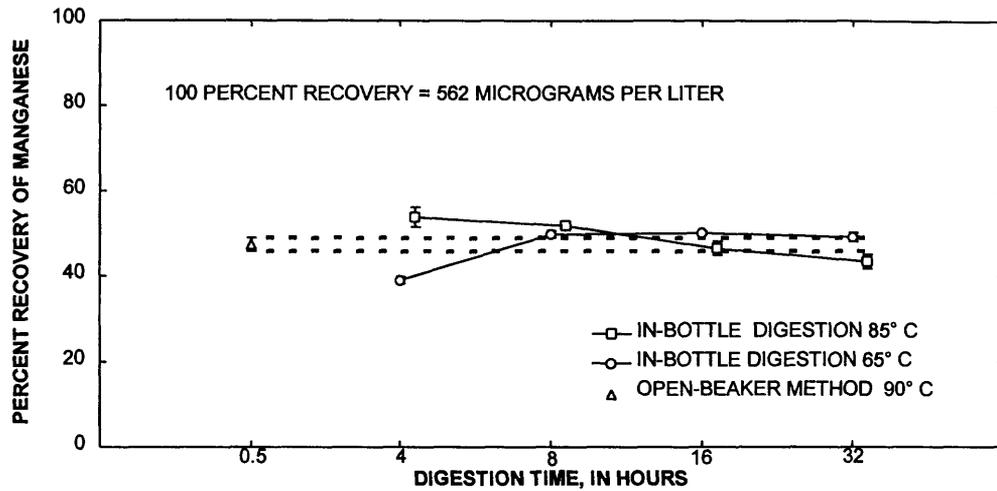(Dashed lines indicate standard deviation for open-beaker method.)

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Figure 11. Acid digestion of synthetic whole-water samples made from estuarine
sediment to determine time and temperature requirements of the in-bottle
method to obtain data equivalent to the open-beaker method for manganese.
(Dashed lines indicate standard deviation for open-beaker method.)
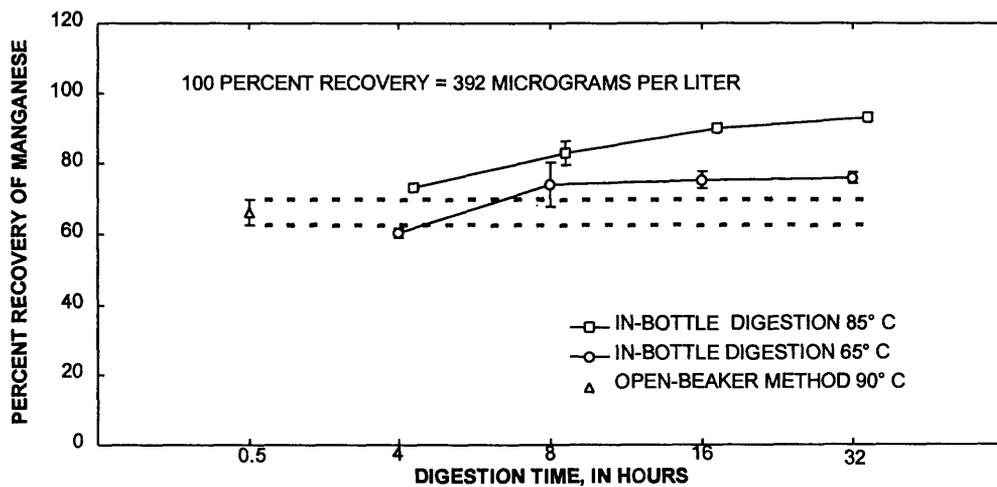


Figure 12. Acid digestion of synthetic whole-water samples made from river sediment
to determine time and temperature requirements of the in-bottle method to
obtain data equivalent to the open-beaker method for manganese.
(Dashed lines indicate standard deviation for open-beaker method.)

Figure 13. Acid digestion of synthetic whole-water samples made from estuarine
sediment to determine time and temperature requirements of the in-bottle
method to obtain data equivalent to the open-beaker method for nickel.
(Dashed lines indicate standard deviation for open-beaker method.)

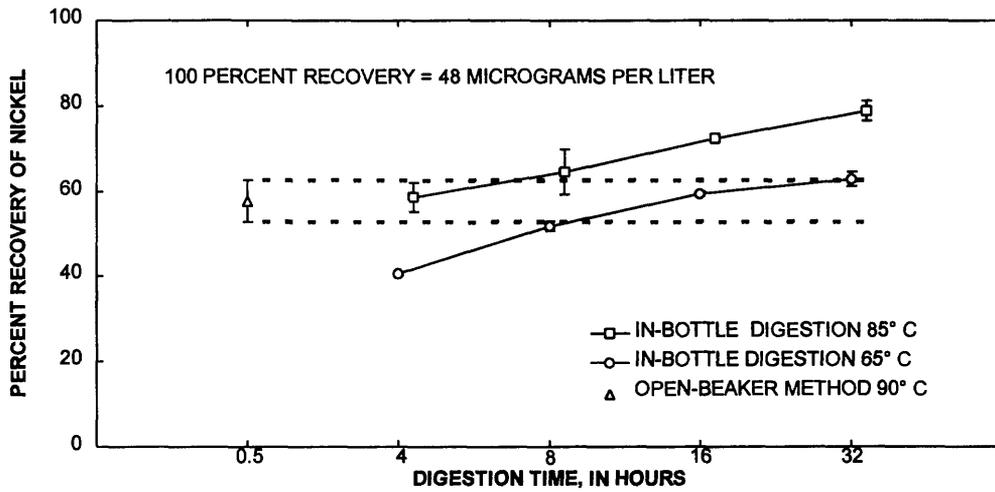

Figure 14. Acid digestion of synthetic whole-water samples made from river
sediment to determine time and temperature requirements of the in-bottle
method to obtain data equivalent to the open-beaker method for nickel.
(Dashed lines indicate standard deviation for open-beaker method.)

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Figure 15. Acid digestion of synthetic whole-water samples made from estuarine
sediment to determine time and temperature requirements of the in-bottle
method to obtain data equivalent to the open-beaker method for zinc.
(Dashed lines indicate standard deviation for open-beaker method.)
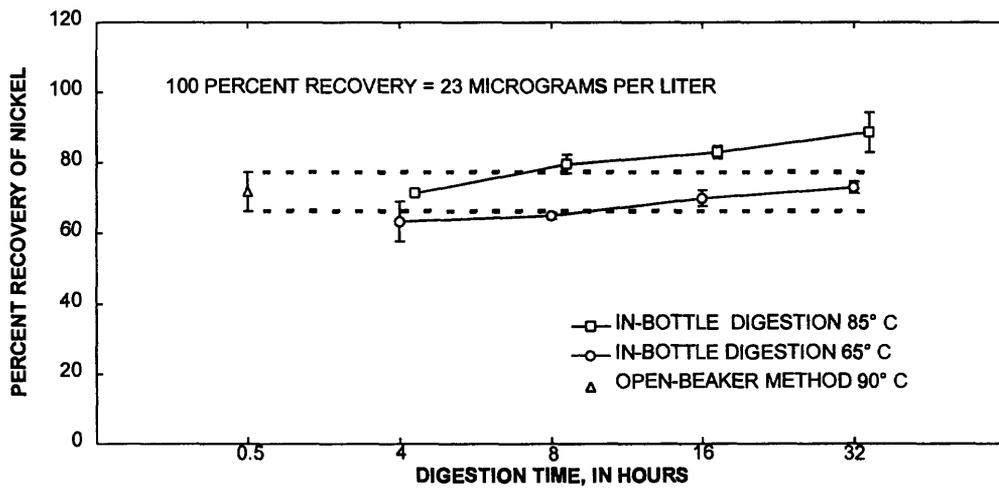


Figure 16. Acid digestion of synthetic whole-water samples made from river
sediment to determine time and temperature requirements of the in-bottle
method to obtain data equivalent to the open-beaker method for zinc.
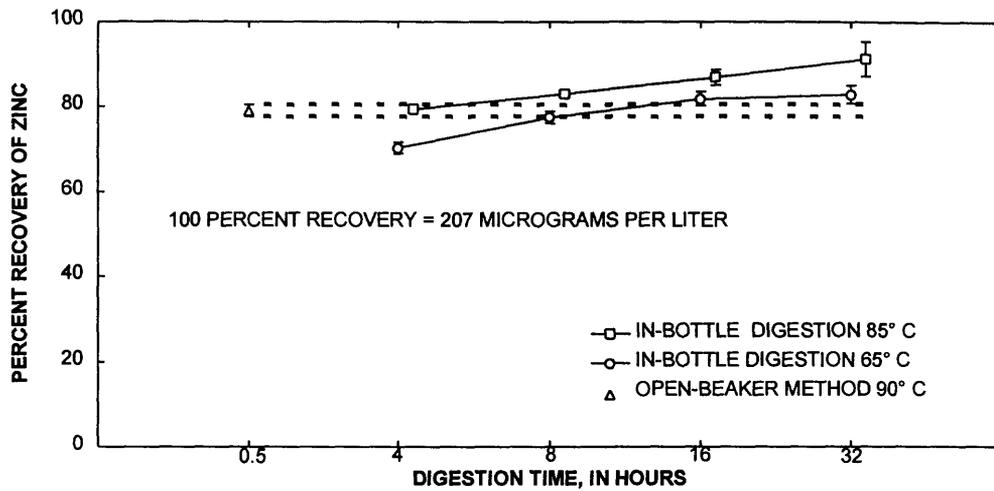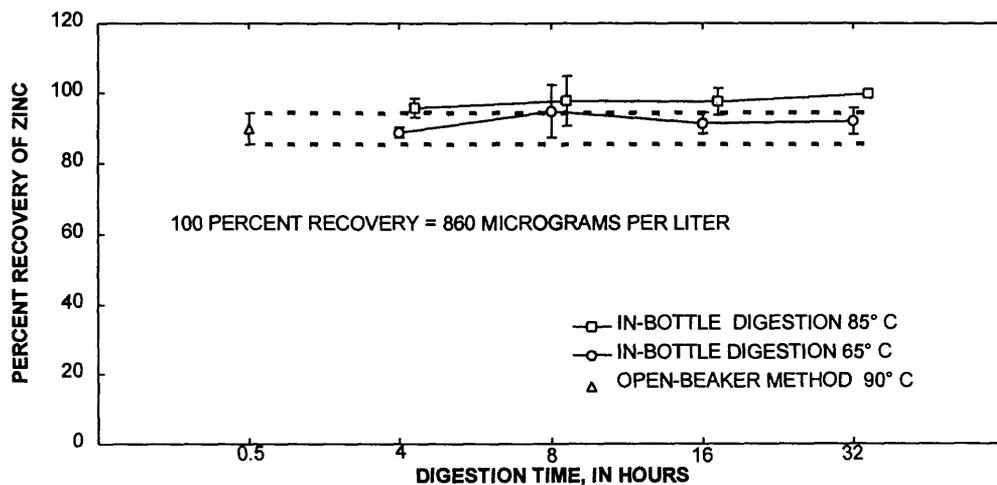(Dashed lines indicate standard deviation for open-beaker method.)

Figure 17. Cadmium data for whole-water samples using in-bottle and open-beaker methods.

Number of samples: 30
Correlation coefficient: r = 0.995
Linear regression: Y = 0.088 + 0.992 X



Figure 18. Cobalt data for whole-water samples using in-bottle and open-beaker methods.

Number of samples: 30
Correlation coefficient: r = 0.978
Linear regression line: Y = -0.072 + 1.02 X

Figure 19. Copper data for whole-water samples using in-bottle and open-beaker methods.



Figure 20. Iron data for whole-water samples using in-bottle and open beaker methods

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Figure 21. Lead data for whole-water samples using in-bottle and open-beaker methods

Number of samples: 30
Correlation coefficient: r = 0.988
Linear regression: Y = 2.09 + 0.993 X



Figure 22. Manganese data for whole-water samples using in-bottle and open-beaker methods.

Number of samples : 30
Correlation coefficient: r = 0.999
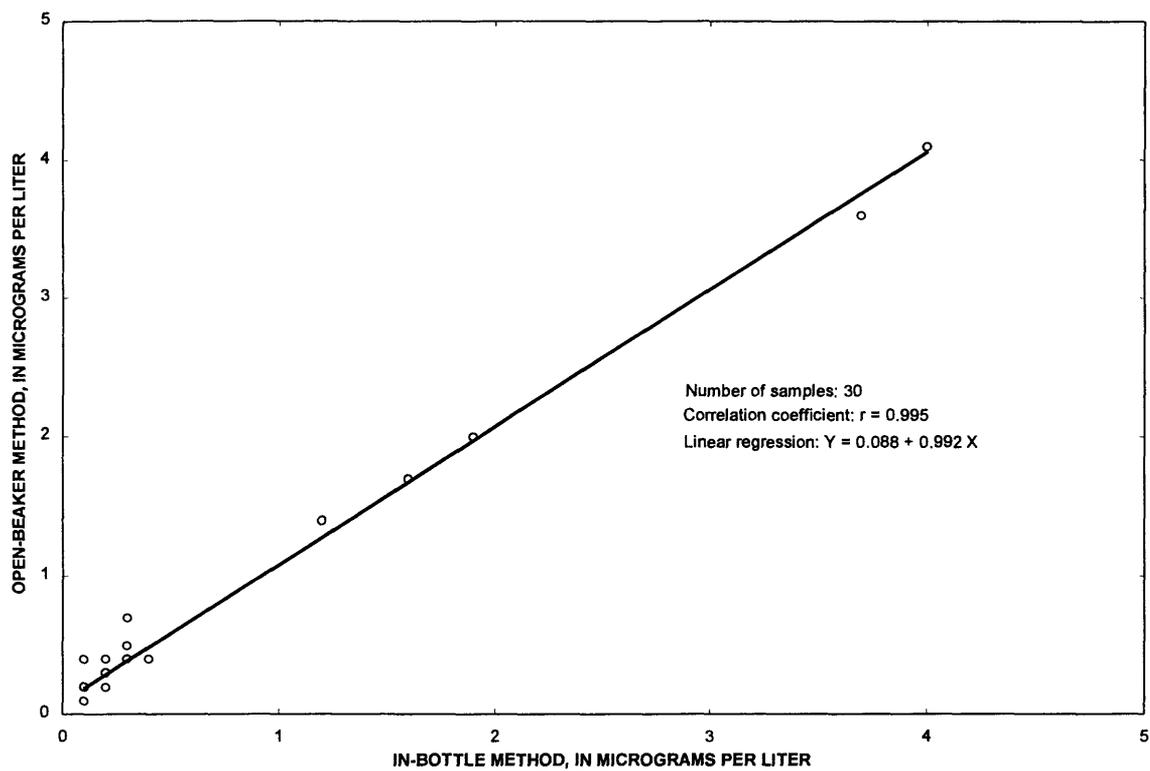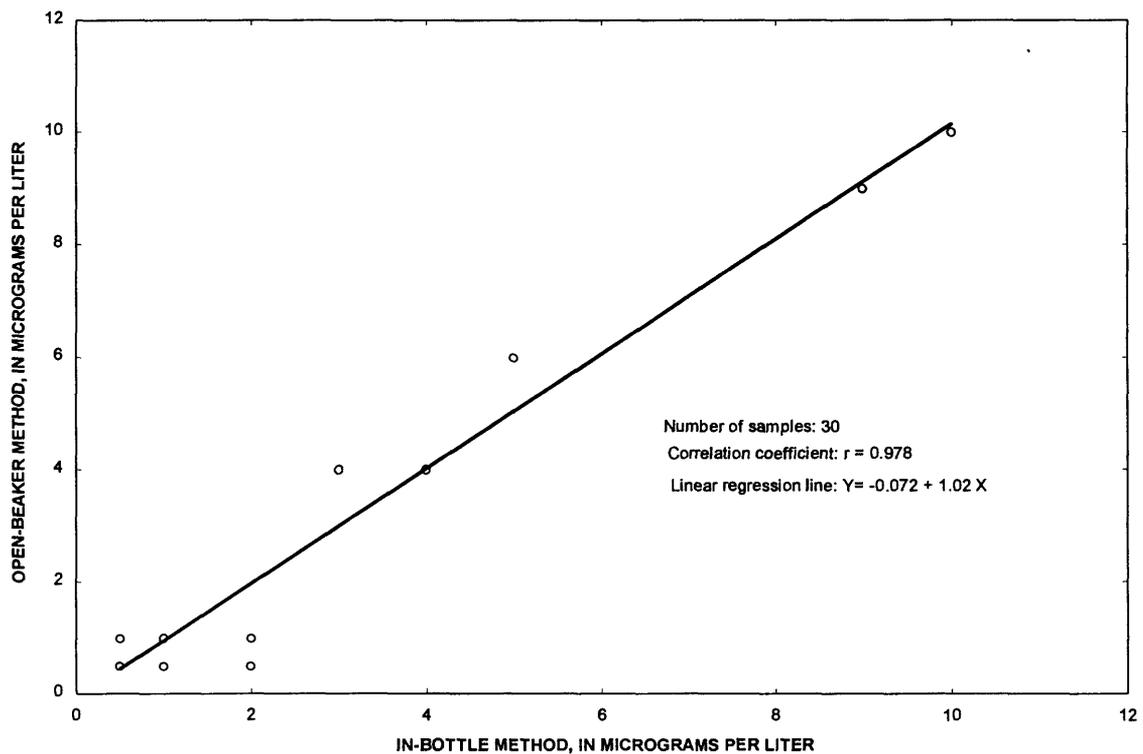Linear regression: Y = 1.67 + 0.980 X

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Figure 23. Nickel data for whole-water samples using in-bottle and open beaker methods.



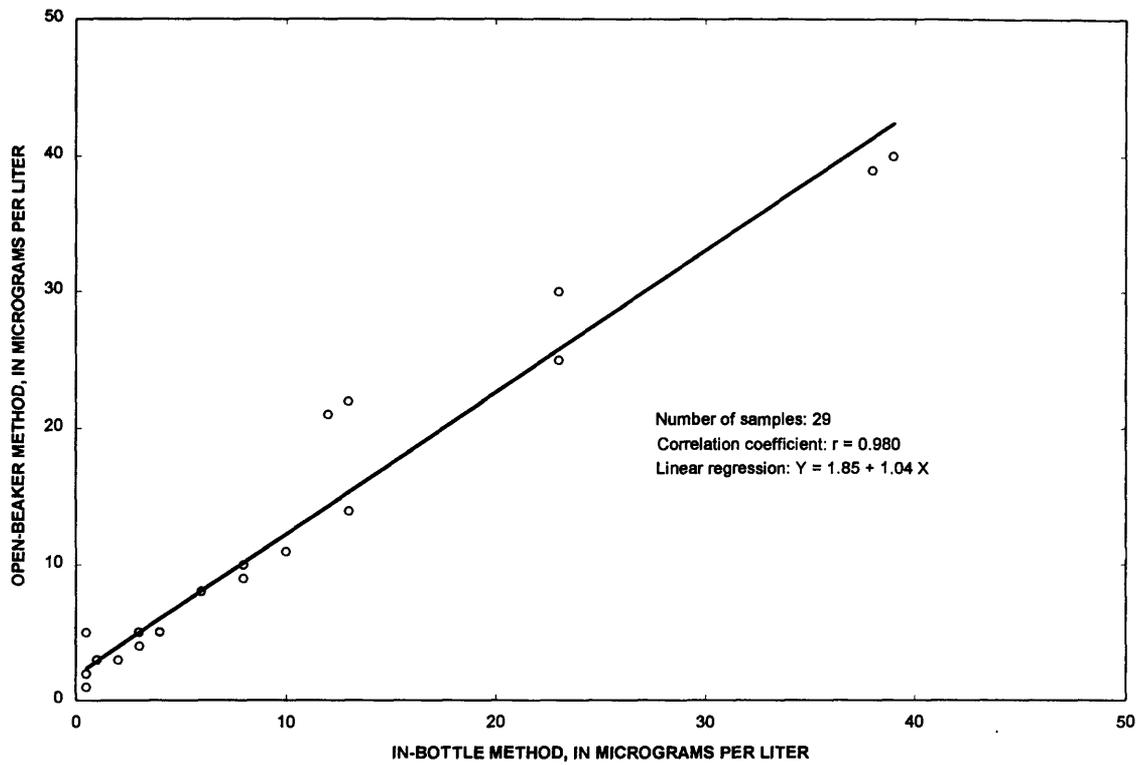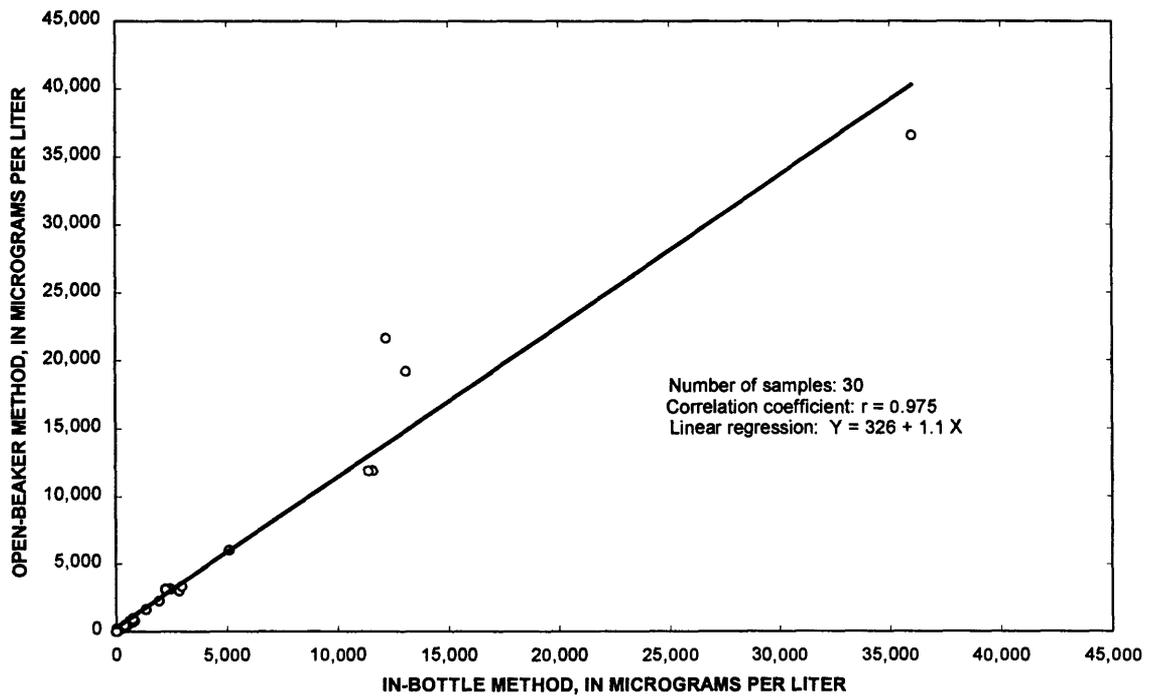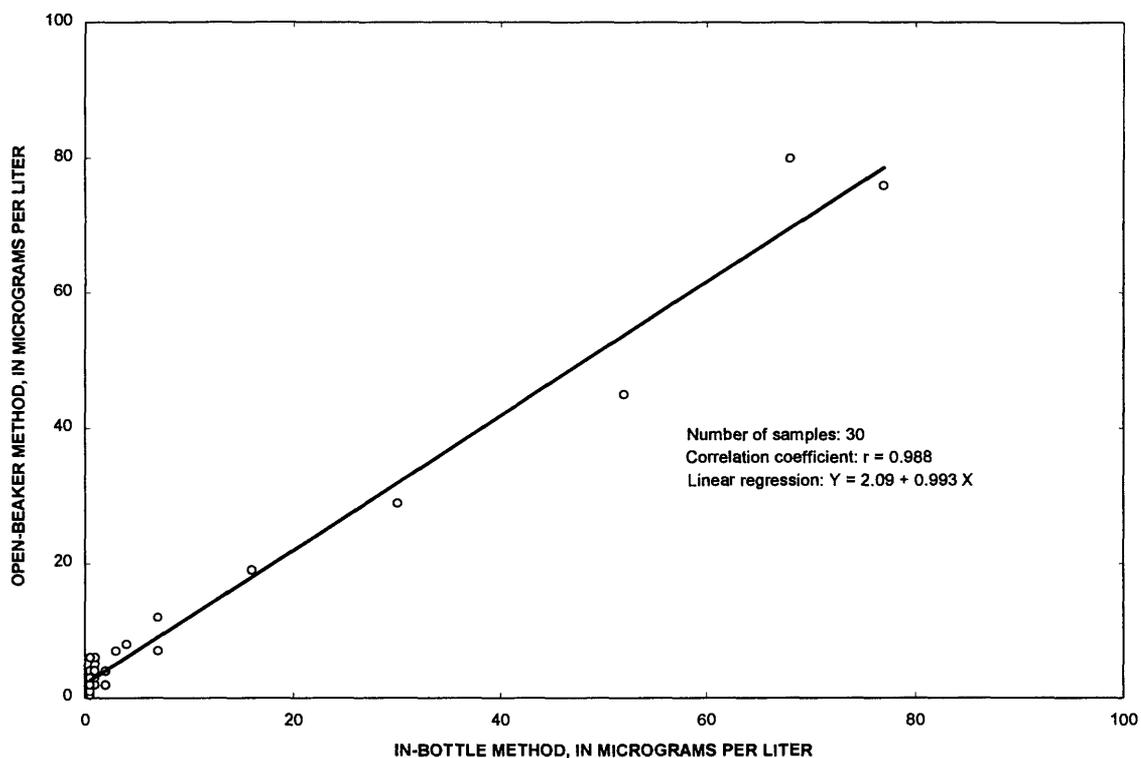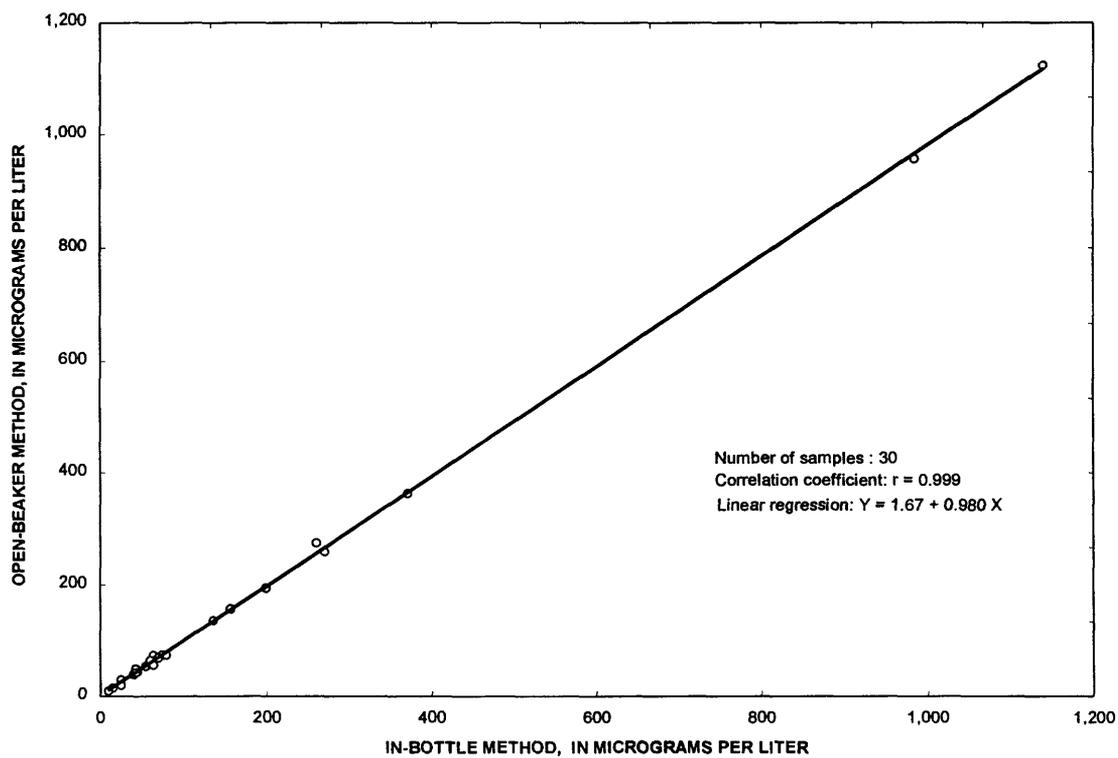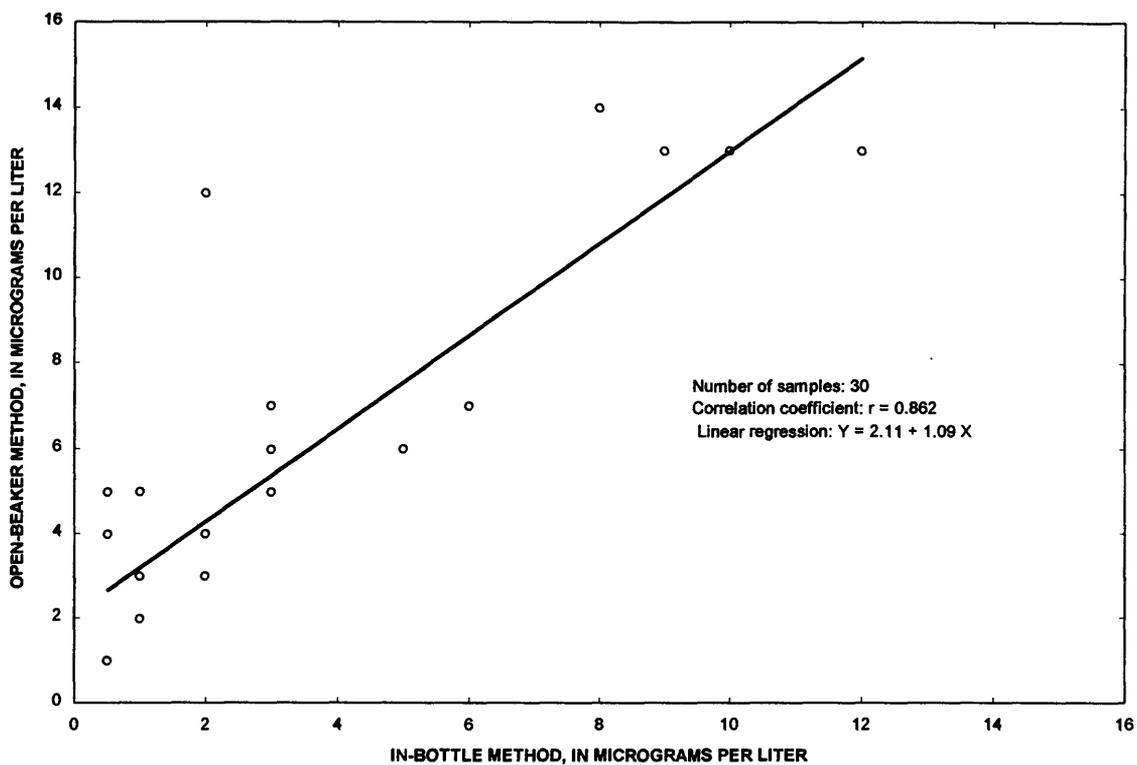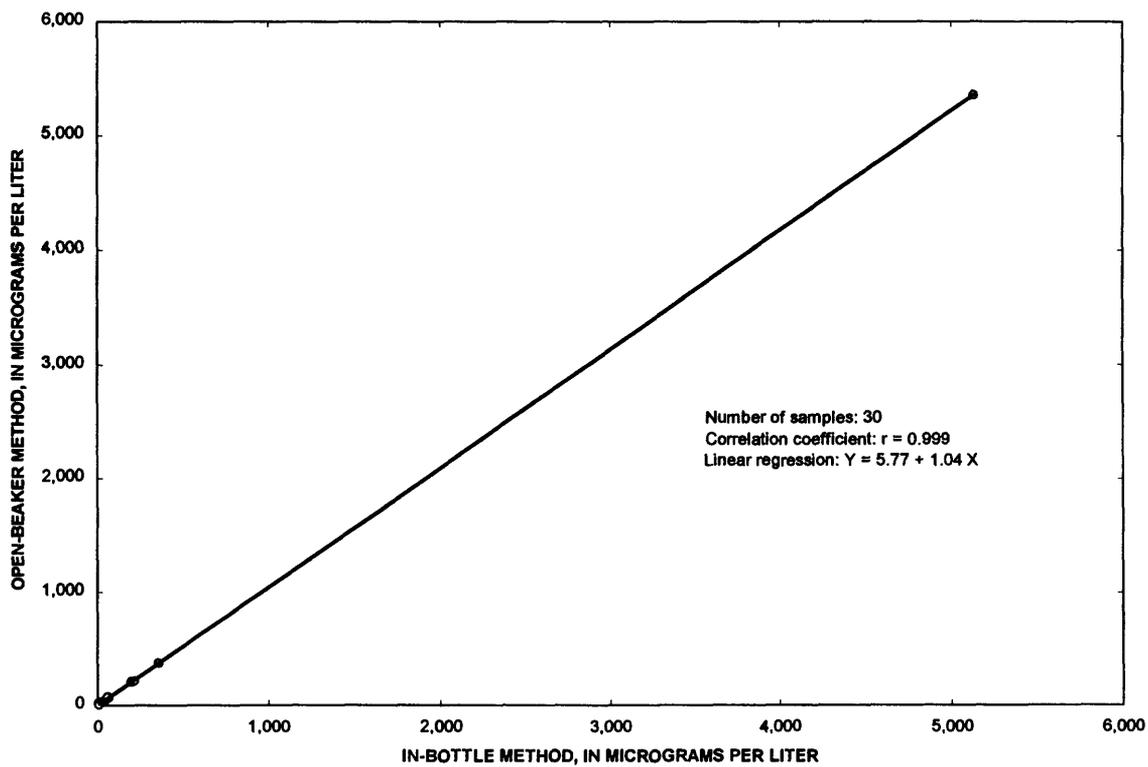Figure 24. Zinc data for whole-water samples using in-bottle and open-beaker methods.

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# APPENDIX B—MODIFICATION OF ORIGINAL IN-BOTTLE DIGESTION CONDITIONS

# Modification of Original In-Bottle Digestion Conditions

The in-bottle digestion procedure was modified as follows after all of the studies were completed: (1) the amount of HCl added to water samples was changed from 2.5 percent (v/v) to 2.0 percent (v/v); and (2) water samples were not filtered 1/2 hour after the 8-hour heating period was completed, but were allowed to stand at room temperature for a minimum of 8 hours (overnight) before the water samples were filtered. The second change was made to the digestion procedure for convenience in processing the samples. Water samples are acidified with HCl in the afternoon and placed in an oven equipped with an automatic timer and heat controls. The oven is activated to start the 8-hour heating process at the end of the work day. After 8 hours of heating, the oven automatically shuts off the heating elements and cools to room temperature. The air temperature inside the oven returns to ambient within 1/2 hour after the heating cycle has stopped. The samples remain inside the oven until the next morning when they are removed and processed using procedures described previously (section 6.7, Sample filtration).

A study was conducted to determine if these two modifications to the original in-bottle (OIB) digestion procedure would significantly change the recovery yields of any metals measured. Synthetic whole-water samples made from NIST reference sediments SRM 1645 (river sediment) and SRM 1646 (estuarine sediment) were used to evaluate differences in metal digestion recoveries for the modified in-bottle (MIB) digestion procedure compared to the OIB digestion procedure. These two types of synthetic water samples are identical to the synthetic water samples used in the original method validation procedures. For a complete description of how these synthetic water samples were made, refer to Discussion of Results section on synthetic whole-water samples.

A total of 32 synthetic whole-water samples (16 river sediment and 16 estuarine sediment) was prepared. Half of the river and estuarine sediment synthetic whole-water samples were digested using the modified conditions and the other half were digested using the original conditions. All samples were analyzed by inductively coupled plasma–mass spectrometry (ICP–MS) and inductively coupled plasma–atomic emission spectrometry (ICP–AES) for the same elements used to establish the conditions for the original in-bottle digestion procedure. The elemental concentrations determined for the synthetic whole-water samples digested with the OIB and MIB are listed in table 3. The percent yield for each of the metals determined was calculated and is listed in table 4. Differences in the precision and means for the metal concentrations measured in the synthetic whole-water samples were determined by applying the F-test and $t$-test to the resultant percent yield data. The statistical tests could not be applied to the concentrations given in table 3 because of the variation in weight of sediment used in each sample. The percent yield data listed in table 4 effectively normalizes the concentrations by dividing by the weight of sediment used for each sample.

The null hypothesis for the $t$-test applied in this study is that there is no difference in the mean metal concentrations measured for MIB and OIB samples. The alternate hypothesis is the means for the two procedures are different. A two-tailed test ($\alpha=0.05$) was used because it was not known if the modified procedure would increase or decrease the metal percent yields for any metal determined. In all cases no significant difference (probability = 95 percent) could be determined, and, therefore, the null hypothesis (no difference in the mean percent recovery) could not be rejected.

**Table 3.** Original in-bottle and modified in-bottle methods using synthetic whole-water samples made from river and estuarine sediment standard reference material

[All concentrations in micrograms per liter. Std. dev., standard deviation; E, estuarine sediment sample; R, river sediment sample]

| Trace metal | Sample type | Preparation method | | | |
|---|---|---|---|---|---|
| | | Original in-bottle method | | Modified in-bottle method | |
| | | Mean percent yield | Std. dev. | Mean percent yield | Std. dev. |
| Cadmium | E | 0.55 | 0.09 | 0.50 | 0.04 |
| Cadmium | R | 4.24 | .15 | 4.31 | .49 |
| Cobalt | E | 8.44 | .25 | 8.44 | .25 |
| Cobalt | R | 2.81 | .34 | 2.64 | .23 |
| Copper | E | 16.3 | 1.1 | 16.1 | 1.5 |
| Copper | R | 51.1 | 5.9 | 53.9 | 7.1 |
| Iron | E | 30,949 | 869 | 32,074 | 1,060 |
| Iron | R | 24,770 | 947 | 24,095 | 1,920 |
| Lead | E | 31.5 | 1.2 | 32.3 | 1.2 |
| Lead | R | 339 | 3 | 340 | 31 |
| Manganese | E | 292 | 8 | 303 | 10 |
| Manganese | R | 267 | 11 | 266 | 22 |
| Nickel | E | 22.0 | .9 | 23.0 | .7 |
| Nickel | R | 15.4 | 1.0 | 14.9 | 1.3 |
| Zinc | E | 157 | 4.6 | 160 | 3.5 |
| Zinc | R | 846 | 32 | 836 | 69 |

The null hypothesis for differences in precision (F-test) for the two digestion procedures is that the metal percent yield variances are equal. A one-tailed test ($\alpha=0.05$) was used because either population (metal percent yields for the MIB or OIB methods) could have a larger variance. Only 4 cases (1 estuary and 3 river sediment whole-water samples) out of 16 comparisons tested showed a significant difference in the precision between the OIB and MIB methods. In all four cases the MIB method had better precision than the OIB method. Cadmium percent yields for the estuary sediment and cobalt, iron, and zinc for the river sediment had a larger variance for the OIB method than for the MIB method. In two instances (iron and zinc for river sediment) the standard deviations for the concentration results listed in table 3 indicate that the OIB method has a smaller variance than the MIB method. However, when the concentrations in table 3 are normalized (table 4) for the weight of sediment used, this conclusion is reversed because the resultant standard deviations for iron and zinc percent yields are smaller for the MIB method.

Two conclusions can be drawn from this study: (1) There is no difference in the mean percent yields for the OIB or the MIB methods; and (2) the MIB method is not less precise than the OIB method.

**Table 4.** Percent yields of original in-bottle and modified in-bottle methods using synthetic whole-water samples made from river and estuarine sediment standard reference material

[Std. dev., standard deviation; E, estuarine sediment sample; R, river sediment sample]

| Trace metal | Sample type | Preparation method | | | |
|---|---|---|---|---|---|
| | | Original in-bottle method | | Modified in-bottle method | |
| | | Mean percent yield | Std. dev. | Mean percent yield | Std. dev. |
| Cadmium | E | 100.8 | 16.2 | 90.0 | 7.65 |
| Cadmium | R | 78.6 | 2.53 | 80.9 | 2.45 |
| Cobalt | E | 52.6 | 1.48 | 53.4 | 1.86 |
| Cobalt | R | 52.5 | 6.48 | 50.0 | .99 |
| Copper | E | 60.6 | 2.70 | 60.9 | 3.22 |
| Copper | R | 84.5 | 8.58 | 87.8 | 8.23 |
| Iron | E | 60.4 | 1.36 | 61.8 | 2.50 |
| Iron | R | 41.4 | 1.09 | 40.9 | .34 |
| Lead | E | 73.0 | 2.33 | 74.0 | 3.65 |
| Lead | R | 89.7ʾ | 2.61 | 91.3 | 2.96 |
| Manganese | E | 50.9 | 1.16 | 52.2 | 2.14 |
| Manganese | R | 64.4 | 1.82 | 65.0 | 1.74 |
| Nickel | E | 45.1 | 1.72 | 46.5 | 2.0 |
| Nickel | R | 63.6 | 4.12 | 62.4 | 2.19 |
| Zinc | E | 74.3 | 1.65 | 75.1 | 2.43 |
| Zinc | R | 92.8 | 2.18 | 93.2 | 1.08 |