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# Project Summary

# A Single-Laboratory Evaluation of SW-846 Methods 7090/7091 Determination of Beryllium by Flame and Furnace Atomic Absorption Spectrophotometry

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**The results of a single-laboratory study of the SW-846 Method 7090/7091—''Determination of Beryllium by Flame and Furnace Atomic Absorption Spectrophotometry'' are described. This study examined the application of these two powerful beryllium detection methods to the analysis of selected liquid and solid samples after digestion by appropriate SW-846 methods. Method performance data, including: detection limits, optimum concentration ranges (linearity), spike recoveries, interferences, precision, accuracy, and optimum instrument operating parameters, are presented and discussed.**

***This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

## Introduction

The single-laboratory evaluation of SW-846 Methods 7090/7091 for the determination of beryllium by flame and furnace atomic absorption spectrophotometry (AAS) was undertaken in order to obtain method-performance data and to augment existing data. The method-performance parameters studied were:

1. Detection Limits
2. Optimum Concentration Ranges (Linearity)
3. Spike Recoveries
4. Interferences
5. Precision
6. Accuracy
7. Ruggedness Testing

All data were collected according to the procedures described in "Guidelines for Selection and Validation of U.S. EPAs Measurement Methods" (Draft, January 30, 1986) and "Test Methods for Evaluating Solid Waste," SW-846 (Third Edition, November 1986).

Method 7090 and Method 7091 are measurement procedures for the determination of beryllium in solution. Therefore, solid waste samples, and most aqueous samples, require digestion prior to analysis. Twelve performance evaluation or target samples were chosen for this study. Five of these were liquid samples, two of which were U.S. National Bureau of Standards—Standard Reference Materials (NBS-SRMS). There were seven solid samples of which two were NBS-SRMS, two were Certified Reference Materials from Canada (one from the National Research Council, Ottawa, and one from the Centre for Mineral and Energy Technology, Ottawa)

and one solid was a U.S. EPA-CLP Reference Material prepared by the UNLV-QAL. The liquid samples to be analyzed by flame AAS (Method 7090) were digested according to Method 3010, and the liquid samples to be analyzed by furnace AAS (Method 7091) were digested according to Method 3020. All solid samples were digested by Method 3050 prior to analyses.

Instrument detection limits and the optimum concentration ranges were determined in aqueous samples that were free from interferences. Method-detection limits, spike recoveries, precision, and accuracy were determined in digests of each of the 12 target samples. The stability of beryllium in the sample digests was monitored for 30 days.

A survey of the literature revealed several reports of elements whose presence in solutions containing beryllium, caused increased or decreased absorbance, thereby giving erroneously high or low concentration measurements for beryllium. Therefore, the individual effects of Al, Mg, and Si on the determination of beryllium by flame AAS (Method 7090) and of Al, Ca, Ce, Cr, La, Mg, Mn, Mo, Si, Sr, $H_2SO_4$, W, and Fe by furnace AAS (Method 7091) were investigated. Several chemicals including hydrofluoric acid, 8-hydroxyquinoline and lanthanum were reported to eliminate some of the interferences. The usefulness of these additives was also investigated.

## Conclusions

The single-laboratory evaluation of Method 7090 and Method 7091 demonstrates that the methods are sensitive, precise, and accurate for the quantification of beryllium in a variety of solutions. The solutions targeted by this study included acid digests of liquid and solid samples according to SW-846 digestion Method 3010, Method 3020, and Method 3050. The performance parameters determined in this study for the two methods are summarized below.

## *Determination of Beryllium by Acetylene/Nitrous Oxide Flame Atomic Absorption Spectrophotometry (Method 7090)*

The instrument detection limit (IDL) for the determination of beryllium by flame AAS in a matrix free from interferences was found to be 0.003 mg/L. The optimum concentration range, also in a matrix free from interferences, was found to be 0.01 mg/L to 2.6 mg/L.

The analysis of the 12 liquid and solid samples that were digested by Method 3010 or Method 3050 yielded a method detection limit (based on 1-g/100 mL for solids) of 0.005 mg/L, or, two times the IDL (Table 1). The percent relative standard deviation (%RSD) was used as a measure of the precision of the method, and it ranged from about five percent at 0.02 mg/L to less than one percent at 0.75 mg/L. Recoveries of predigestion spikes of beryllium at 0.25 mg/L and 0.50 mg/L averaged 89 percent (99 percent with the addition of 0.1 percent hydrofluoric acid (Table 2).

Aluminum was found to be the only element, of the five investigated, that interfered with the determination of beryllium (40 percent depression of absorbance at 1000 mg/L and 54 percent at 5000 mg/L). The addition of 0.1 percent hydrofluoric acid or 2.5 percent 8-hydroxyquinoline were found to be effective in eliminating this interference for concentrations of aluminum up to 1000 mg/L. The addition of 0.3 percent hydrofluoric acid was effective in eliminating the interference of aluminum at 5000 mg/L. By using modern instrumentation, high concentrations of Mg and Si (up to 5000 mg/L) did not interfere with the determination of beryllium as currently stated in Method 7090.

The accuracy of Method 7090 was evaluated by determining the beryllium concentration in three NBS-SRMs, before and after digestion by SW-846 methods, with excellent results.

## *Determination of Beryllium by Furnace Atomic Absorption Spectrophotometry (Method 7091)*

The instrument detection limit for beryllium in a matrix free from interferences was found to be 0.08 µg/L (Table 3). The optimum concentration range, also in a matrix free from interferences, was found to be from 0.01 µg/L to 16 µg/L.

The analysis of 12 liquid and solid samples, which were digested by Method 3020 or Method 3050, yielded a method detection limit of 0.08 µg/L, the value of which is the same as the instrument detection limit, demonstrating that a variety of matrices had little or no effect on the detection of beryllium. The percent RSD was used as a measure of the precision and ranged from an average of 7 percent at concentrations below 3 µg/L to an average of 2.3 percent at concentrations above 3 µg/L. Recoveries of predigestion spikes of beryllium at 2.5 µg/L and 5.0 µg/L averaged 93 percent.

A literature survey suggested that the presence of any one of 12 elements can enhance or depress the absorbance of beryllium in the furnace analysis. However, it was found that when peak area was used to calculate the concentration

*Table 1. Method Detection Limit for the Determination of Beryllium by Flame Atomic Absorption Spectrophotometry, Method 7090*

| Matrix | Slope[a] | MDL (µg/L)[a] |
|---|---|---|
| *Trace Elements in Water* | 0.92 | 4.4 |
| *Beryllium Spectrometric Solution* | 0.90 | 4.4 |
| *Synthetic Interference Solution* | 0.54 | 7.4 |
| *Natural Waste Water* | 0.90 | 4.5 |
| *TCLP Extract of Hazardous Waste* | 0.94 | 4.0 |
| *Coal Fly Ash* | 0.77 | 5.2 |
| *Municipal Digested Sludge* | 0.73 | 5.4 |
| *Three Kids Mine Material* | 0.64 | 6.3 |
| *Marine Sediment* | 0.74 | 5.4 |
| *Mineral Sample* | 0.68 | 5.9 |
| *Hazardous Waste Site Soil* | 0.73 | 5.5 |
| *Copper-Beryllium Alloy* | 0.90 | 4.4 |
| *Average* | 0.78 | 5.2 |

[a] *The method detection limit is defined by MDL = 3 $S_B/m$, where $S_B$ is the standard deviation of the instrument background signal and m is the slope of the calibration line in the sample matrix.*

**Table 2.** *Predigestion Spike Recoveries of Beryllium Determined by Flame Atomic Absorption Spectrophotometry, Method 7090, After Digestion of Liquids by Method 3010 and Solids by Method 3050*

| | Be Added (mg/L) | Percent Recovery Without HF | Percent Recovery With HF[a] |
|---|---|---|---|
| Trace Elements in Water | 0.250 | 112 | 109 |
| | 0.500 | 106 | 103 |
| Beryllium Spectrometric Solution | 0.250 | 104 | 106 |
| | 0.500 | 106 | 105 |
| Synthetic Interference Solution | 0.250 | 78 | 104 |
| | 0.500 | 87 | 104 |
| Natural Waste Water | 0.250 | 67 | 105 |
| | 0.500 | 106 | 106 |
| TCLP Extract of Hazardous Waste | 0.250 | 101 | -- |
| | 0.500 | 95 | -- |
| Coal Fly Ash | 0.250 | 97 | 98 |
| | 0.500 | 87 | 96 |
| Municipal Digested Sludge | 0.250 | 86 | 85 |
| | 0.500 | 83 | 82 |
| Three Kids Mine Material | 0.250 | 78 | 101 |
| | 0.500 | 74 | 97 |
| Marine Sediment | 0.250 | 85 | 98 |
| | 0.500 | 82 | 97 |
| Mineral Sample | 0.250 | 78 | 89 |
| | 0.500 | 79 | 87 |
| Hazardous Waste Soil | 0.250 | 85 | 103 |
| | 0.500 | 83 | 101 |
| Copper-Beryllium Alloy | 0.500 | 98 | 99 |
| | 1.000 | 96 | 96 |

[a]*With the addition of 0.1 percent HF.*

**Table 3.** *Method Detection Limit for the Determination of Beryllium by Furnace Atomic Absorption Spectrophotometry, Method 7091*

| Matrix | Slope[a] | MDL (µg/L)[a] |
|---|---|---|
| Trace Elements in Water | 0.99 | 0.08 |
| Beryllium Spectrometric Solution | 0.95 | 0.08 |
| Synthetic Interference Solution | 1.01 | 0.08 |
| Natural Waste Water | 1.06 | 0.08 |
| TCLP Extract of Hazardous Waste | 1.08 | 0.07 |
| Coal Fly Ash | 0.99 | 0.08 |
| Municipal Digested Sludge | 0.93 | 0.09 |
| Three Kids Mine Material | 0.96 | 0.08 |
| Marine Sediment | 0.94 | 0.08 |
| Mineral Sample | 0.97 | 0.08 |
| Hazardous Waste Site Soil | 0.94 | 0.09 |
| Copper-Beryllium Alloy | 0.85 | 0.09 |
| Average | 0.97 | 0.08 |

[a]*The method detection limit is defined by MDL = 3 $S_B/m$, where $S_B$ is the standard deviation of the instrument background signal and m is the slope of the calibration line in the sample matrix.*

of beryllium in the presence of these elements, only molybdenum interfered with the determination of beryllium (Table 4). The presence of 1000 mg/L molybdenum enhanced the peak area of a 5 µg/L solution of beryllium by 20 percent.

The accuracy of Method 7091 was evaluated by determining the concentration of beryllium in three NBS-SRMS before and after digestion by SW-846 Methods, with excellent results.

## Recommendations

The following recommendations are listed by method, with section references made to the method as written in SW-846.

## *Method 7090*

### 3.0 Interferences

3.2 This section states that "Background correction may be required. . ." This statement should be modified to read "Background correction *is* required. . ."

3.3 This section warns that "Concentrations of aluminum greater than 500 ppm may suppress beryllium absorbance." This statement should be modifed to read "Concentrations of aluminum greater than *100* mg/L will suppress beryllium absorbance." The addition of 0.1 percent hydrofluoric acid was found to be effective in eliminating this interference as stated in the current version of the method. However, this study demonstrated that 0.3 percent hydrofluoric acid is required for aluminum concentrations greater than 1000 mg/L.

With regard to the statement, "High concentration of magnesium and silicon. . ." no evidence was obtained to corroborate this statement; no significant interferences from Mg or Si at concentrations up to 5000 mg/L were observed in this single-laboratory study using modern instrumentation. Therefore, it is recommended that this sentence be deleted.

### 9.0 Method Performance

9.1 While the results of this study yielded somewhat different values for the optimum concentration range and detection limit, the values currently cited in Method 7090 are near the experimental levels found in this study. Therefore, no changes are recommended for this section.

*Table 4. Effect of Aluminum, Calcium, Cerium,Chromium, Lanthanum, Magnesium, Manganese, Molybdenum, Silicon, Strontium, Sulfuric Acid, Tungsten, and Iron on the Observed Absorbance of Beryllium in Furnace Atomic Absorption Spectrophotometry, Method 7091*

| Interfering Element (mg/L) | Observed Be Absorbance in Presnce of these Chemicals[a] | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Al | Ca | Ce | Cr | La | Mg | Mn | Mo | Si | Sr | $H_2SO_4$ | W | Fe |
| *Peak Area* | | | | | | | | | | | | | |
| 0 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 |
| 100 | 0.424 | 0.452 | 0.430 | 0.419 | 0.457 | 0.470 | 0.458 | 0.431 | 0.434 | 0.460 | 0.446 | 0.370 | 0.435 |
| 500 | 0.444 | 0.430 | 0.430 | 0.414 | 0.449 | 0.475 | 0.464 | 0.467 | 0.437 | 0.450 | 0.428 | 0.363 | 0.427 |
| 1000 | 0.421 | 0.423 | 0.406 | 0.408 | 0.443 | 0.468 | 0.466 | 0.513 | 0.435 | 0.445 | 0.432 | 0.343 | 0.433 |
| 5000 | 0.400 | 0.452 | 0.388 | 0.387 | 0.438 | 0.484 | 0.467 | 0.805 | 0.408 | 0.448 | 0.427 | 0.330 | 0.430 |
| *Peak Height* | | | | | | | | | | | | | |
| 0 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 | 0.427 |
| 100 | 0.398 | 0.524 | 0.432 | 0.445 | 0.476 | 0.620 | 0.465 | 0.431 | 0.433 | 0.494 | 0.473 | 0.378 | 0.558 |
| 500 | 0.498 | 0.719 | 0.517 | 0.578 | 0.722 | 0.846 | 0.452 | 0.465 | 0.442 | 0.638 | 0.458 | 0.387 | 0.520 |
| 1000 | 0.474 | 0.755 | 0.657 | 0.587 | 0.901 | 0.841 | 0.455 | 0.504 | 0.449 | 0.688 | 0.451 | 0.372 | 0.544 |
| 5000 | 0.479 | 1.074 | 0.551 | 0.495 | 0.621 | 0.715 | 0.703 | 0.777 | 0.437 | 0.978 | 0.431 | 0.349 | 0.491 |

[a]*Data has been normalized.*

## *Method 7091*

### 3.0 Interferences

3.2 The results obtained in this study document that the method is essentially free from interferences from 10 of the 11 elements tested. Only molybdenum produced an interference, enhancing the absorbance at concentrations of 1000 mg/L and above. Section 3.2 should be modified to read "Chemical and physical interferences can be minimized by optimizing the furnace AAS parameters and by using peak area instead of height in concentration calculations."

### 4.0 Apparatus and Materials

4.2 Instrument Parameters (general). It is recommended that this section be titled: "Instrument Parameters (with pyrolytically coated platform supported by an uncoated graphite tube)."

The following conditions are recommended:

| | Time(s) | | Temp. (°C) |
|---|---|---|---|
| | Ramp | Hold | |
| 4.2.1 Drying | 5 | 25 | 200 |
| 4.2.2 Ashing | 5 | 25 | 900 |
| 4.2.3 Atomizing | 0 | 4 | 2700 |
| 4.2.4 Cleaning | 1 | 1 | 2700 |

The following rewording in the "NOTE:" is suggested:

> "NOTE: The above instrument conditions are for a Perkin-Elmer HGA-500 graphite furnace equipped with an AS-40 Auto Sampler. Concentration values are based on a 10 µL injection with stop-flow at atomization and use of a pyrolytically coated graphite platform. Instruments made by different manufacturers may require a differnt set of conditions."

### 9.0 Method Performance

The following changes are recommended to make the sections in Method 7090 and Method 7091 similar.

9.1 The performance characteristics for an aqueous sample free of interferences are:

> Optimum concentration range: 0.1 µg/L-16 µg/L
>
> Sensitivity: 0.4 µg/L
>
> Detection Limit: 0.08 µg/L

9.2 In a single-laboratory analysis of liquid and solid materials prepared by Method 3020 or Method 3050, with beryllium concentrations below 3 µg/L, the %RSD averaged 7 percent. For samples with beryllium concentrations above 3 percent, the %RSD was 2.3 percent. Spike recoveries average 93 percent.

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*The complete report, entitled "A Single-Laboratory Evaluation of SW-846 Methods 7090/7091 Determination of Beryllium by Flame and Furnace Atomic Absorption Spectrophotometry," (Order No. PB 88-171 434/AS; Cost: $19.95, subject to change) will be available only from:*

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