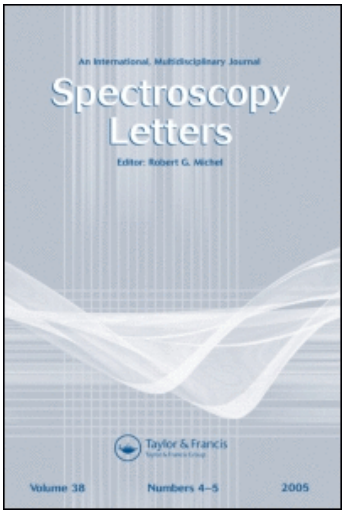

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Determination of Trace Elements in Biological Standard Reference Materials by Graphite Furnace Atomic Absorption Spectrometry with Solid and Slurry Sampling

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DETERMINATION OF TRACE ELEMENTS IN BIOLOGICAL STANDARD REFERENCE MATERIALS BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY WITH SOLID AND SLURRY SAMPLING

Key words: Graphite furnace atomic absorption spectrometry, Slurry sampling, Solid sampling, Biological standard reference materials.

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ABSTRACT

Compared to conventional dissolution methods, solid and slurry sampling methods offer advantages which include speed, improved sensitivity, a reduced risk of contamination, and a reduced risk of analyte loss. Most successful graphite furnace atomic absorption spectrometry

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(GFAAS) results have been obtained by the use of modern furnace technology, which includes Zeeman background correction, platform atomization, and matrix modifiers. In this work, solid and slurry sampling were investigated for the determination of Ag, Cu, Fe, Mn, Pb, and Zn in biological National Institute of Standards and Technology (NIST) standard reference materials (SRMs) with the use of vintage (1980) GFAAS instrumentation, aqueous calibration, and deuterium arc background correction. Although reasonable accuracy was obtained with solid sampling, the relative standard deviation was between 13 and 53 %, which was probably caused by the inability of the furnace to reproducibly vaporize the sample and the inability of deuterium arc background correction to account for the high background signals. Good accuracy and precision (3 - 13 %) were obtained with slurry sampling, with the exception of the determination of copper in citrus leaves. This low result (three times below the certified value) and high precision (RSD = 31 %) were probably caused by irreproducible atomization of the sample matrix.

INTRODUCTION

Conventional methods of sample introduction for graphite furnace atomic absorption spectrometry (GFAAS) include dry ashing, wet oxidation, and fusion fluxing. These dissolution methods have the advantage that a homogeneous solution is produced, which often allows good precision to be obtained, but there are a number of disadvantages associated with these techniques (1). First, the dissolution procedure frequently requires more time than the GFAAS analysis. Another

disadvantage is the possible contamination of the sample caused by the addition of the reagents required for dissolution. Other disadvantages include possible losses of analyte due to retention by insoluble residues or evaporation of volatile elements during the digestion procedure.

Alternative methods of sample introduction include solid or slurry sampling (1-4). Solid sampling is the direct introduction of a solid material into the graphite furnace, while slurry sampling involves the introduction of a powdered material that has been suspended in a liquid diluent. The principal advantage of these techniques is the elimination of a dissolution step which reduces analysis time. In addition, solid and slurry sampling often require less dilution of the sample, which may allow the determination of lower concentrations of analyte, and hence lower the detection limit. These methods employ no reagents (solid sampling) or a reduction in the quantity of reagents (slurry sampling), which decreases the risk of contamination. These simpler methods of sample introduction also have the advantage that there is a reduced risk of analyte lost in the sample introduction step.

Previous work involving solid and slurry sampling for GFAAS has been reviewed by Langmyr and Wibetoe (2), Bendicho and de Loos-Vollebregt (3), de Benzo et al. (4), and Byrd (5). In general, successes in solid and slurry sampling have employed modern furnace technology, which involves the use of Zeeman background correction, platform atomization, and matrix modifiers. In this work, a vintage GFAAS instrument equipped with deuterium arc background correction was used to determine elements in a variety of National Institute of Standards and Technology (NIST) standard reference materials (SRMs) by GFAAS with aqueous calibration and solid and slurry sampling. Solid samples (1-4

mg) were weighed on a probe that was introduced into the furnace. Slurried samples were prepared by use of a vortex mixer to form homogeneous suspensions which were manually pipetted into the furnace. This research was focused on the development of rapid methods of sample preparation for the determination of copper, lead, manganese, iron, zinc, and silver by GFAAS with inexpensive, widely available instrumentation.

EXPERIMENTAL

GFAAS Instrumentation

An Instrumentation Laboratory 551 atomic absorption spectrometer, equipped with an Instrumentation Laboratory 655 graphite furnace and deuterium arc (continuum source) background correction, was used for the GFAAS analyses. Solid sampling was performed with pyrolytically coated solid sampling furnaces (Thermo Jarrell Ash #043988-00) and pyrolytically coated solid sampling boats (Thermo Jarrell Ash #044119-00). Slurry sampling was performed with pyrolytically coated delayed atomization cuvettes (Thermo Jarrell Ash #124271-00).

Preparation of Standards and Samples

Aqueous standards were made by serial dilution of 1 g/L stock solutions of the analyte. All glassware and plasticware were soaked in 2 % nitric acid for at least 12 hours and rinsed with deionized water before use.

TABLE 1. GFAAS Heating Programs employed for Solid Sampling.*

Heating Step	Element†	Temperature, °C	Ramp Time, s	Hold Time, s
Dry 1	All	70	25	0
Dry 2	All	110	40	0
Atomization	Ag	1700	0‡	5
	Cu	2000		
	Mn	2700		
	Pb	1600		

*No char step was employed; see text for explanation.
†Identical dry steps were employed for all elements.
‡Maximum power heating.

The following National Institute of Standards and Technology (NIST) standard reference materials (SRMs) were employed in this research: bovine liver (SRM 1577a), citrus leaves (SRM 1572), non-fat milk powder (SRM 1549), oyster tissue (SRM 1566a), pine needles (SRM 1575), and tomato leaves (SRM 1573). All SRMs were dried at 80°C for two hours prior to use, but were not subjected to any additional grinding or sieving.

Solid samples were prepared by weighing 1 - 4 mg of sample into a previously tared sampling boat, which was then inserted into the solid sampling furnace. We found that it was necessary to rezero the instrument after every furnace firing in order to obtain accurate results.

Slurried samples were prepared using a modification of the vortex method developed by Miller-Ihli (1). 10 - 30 mg of SRM were introduced

into a polypropylene test tube to which 5 - 15 mL of 5 % nitric acid, containing 0.04 % Triton X-100, was added. A vortex mixer was used to produce a slurry of the material. A 20 µL aliquot was then manually injected into the furnace.

The concentrations of elements in the samples were calculated by use of an aqueous calibration curve. All samples were analyzed five times (n = 5). The use of palladium as a matrix modifier was attempted in this work, but its use was discontinued because it severely degraded the precision of aqueous standards.

RESULTS AND DISCUSSION

Temperature Optimization and Spectroscopic Conditions

Char and atomization temperature optimization were performed for all elements for solid and slurry sampling, and the results are summarized in Tables 1 and 2. Identical drying steps were used for all elements with solid and slurry sampling. A char step was not employed for the solid sampling work because very poor precision (> 100 %) was obtained that was probably caused by premature vaporization of analyte. Spectroscopic conditions for the analyses are listed in Table 3.

Solid Sampling Analyses

A summary of our GFAAS analyses of NIST SRMs with solid sampling is listed in Table 4. Relatively few analyses were performed with solid sampling because it is impossible to dilute the samples, and the concentrations of most elements in the samples were not on the linear

TABLE 2. GFAAS Heating Programs employed for Slurry Sampling.

Heating Step	Element*	Temperature, °C	Ramp Time, s	Hold Time, s
Dry 1	All	70	25	0
Dry 2	All	110	40	0
Char	Ag	700	15	15
	Cu	900		
	Fe	1200		
	Mn	1000		
	Pb	900		
	Zn	900		
Atomization	Ag	1400	0†	5
	Cu	1700		
	Fe	2100		
	Mn	2000		
	Pb	1600		
	Zn	1800		

*Identical dry steps were employed for all elements.
†Maximum power heating.

TABLE 3. Spectroscopic Conditions Employed for GFAAS

Element	Wavelength, nm	Hollow cathode lamp current, mA	Photomultiplier tube voltage, V
Ag	328.1	3	700
Cu	324.7	5	800
Fe	248.3	8	900
Mn	279.5	5	800
Pb	283.3	5	800
Zn	213.9	3	800

TABLE 4. Determination of Elements in NIST SRMs by GFAAS with Solid Sampling. Each sample was analyzed five times (n = 5).

Element	Sample	Result by Solid Sampling, µg/g	RSD, %	Certified Value, µg/g
Ag	Bovine Liver	0.032 ± 0.01	31	0.040 ± 0.010
Cu	Milk Powder	0.69 ± 0.09	13	0.7 ± 0.1
Mn	Milk Powder	0.22 ± 0.09	41	0.26 ± 0.06
Pb	Citrus Leaves	0.62 ± 0.33	53	0.135 ± 0.015
	Milk Powder	0.26 ± 0.11	42	0.019 ± 0.003
	Pine Needles	0.43 ± 0.13	30	0.371 ± 0.014

Furnace programs and spectroscopic conditions employed are listed in Tables 1 and 3.

portion of the GFAAS calibration curve. In general, the accuracy of the analyses was reasonably good, except for the determinations of lead, but the precision was poor, with values between 13 and 53 %. This furnace was apparently unable to reproducibly vaporize solid materials, probably because of the absence of modern furnace technology and the inability of deuterium arc background system to correct for the large background signals produced in solid sampling. The high results obtained for the determination of lead were also probably caused by poor correction for background signals. Wagley et al. (6) determined a number of elements in milk powder by GFAAS with solid sampling and modern furnace technology (Zeeman background correction, platform atomization, and a matrix modifier), and obtained RSD values between 7 and 29 %. Although the precision of our solid sampling determinations was relatively high, our results are within a factor of two of measurements made with modern instrumentation.

Slurry Sampling Analyses

Our GFAAS analyses of NIST SRMs by GFAAS with slurry sampling are listed in Table 5. Six elements were determined in a variety of food and agricultural SRMs. With one exception, good agreement was obtained with the certified values, and RSD values were between 3 and 13 %. The exception was the determination of copper in citrus leaves, for which the slurry sampling result was a factor of three lower than the certified value, with an RSD of 31 %. Miller-Ihli (1) accurately determined copper in citrus leaves by use of the vortex slurry method and modern

TABLE 5. Determination of Elements in NIST SRMs by GFAAS with Slurry Sampling. Each sample was analyzed five times (n = 5).

Element	Sample	Result by Slurry Sampling, µg/g	RSD, %	Certified Value, µg/g
Ag	Oyster Tissue	1.79 ± 0.05	3	1.68 ± 0.15
Cu	Bovine Liver	146 ± 17	12	158 ± 7
	Citrus Leaves	5.5 ± 1.7	31	16.5 ± 1.0
	Milk Powder	0.68 ± 0.02	3	0.7 ± 0.1
	Pine Needles	2.9 ± 0.3	10	3.0 ± 0.3
	Tomato Leaves	10.1 ± 0.5	5	11.0 ± 1.0
Fe	Bovine Liver	183 ± 12	7	194 ± 20
	Citrus Leaves	92 ± 12	13	90 ± 10
	Pine Needles	201 ± 11	5	200 ± 10
Mn	Bovine Liver	9.3 ± 0.4	4	9.9 ± 0.8
	Citrus Leaves	21.1 ± 1.3	6	23 ± 2
Pb	Bovine Liver	6.2 ± 0.5	8	6.3 ± 0.3
	Citrus Leaves	11.5 ± 1	9	13.3 ± 2
	Pine Needles	11.2 ± 1	9	10.8 ± 0.5
Zn	Bovine Liver	46 ± 4	9	46 ± 2
	Citrus Leaves	31 ± 2	6	29 ± 2

Furnace programs and spectroscopic conditions employed are listed in Tables 2 and 3.

furnace technology, including Zeeman background correction and platform atomization. This result seems to indicate that the reason for our poor results is the inability of our furnace system to atomize all of the copper from the sample, rather than inhomogeneity of the slurry caused by the location of copper in large particles which quickly settle out of suspension. Miller-Ihli (1) reported that the vortex slurry method gave poor results for iron because of this element's distribution in large particles which rapidly drop out of solution in the autosampler cup. We obtained good results for iron, probably because we employed manual pipetting, which reduced the time available for these particles to settle out of solution.

CONCLUSIONS

Several metals were determined in a variety of NIST SRMs by GFAAS using a vintage spectrometer with solid and slurry sampling and aqueous calibration. Although reasonable accuracy was obtained with solid sampling, the RSD of these measurements was very high, with values between 13 and 53 %. The poor RSD can be attributed to the use of older instrumentation, which was unable to reproducibly atomize the sample and correct for large background signals. In general, slurry sampling gave good accuracy and precision, with RSD values between 5 and 14 %. The determination of copper in citrus leaves gave poor results by slurry sampling, probably because the older furnace could not reproducibly atomize the sample matrix.

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REFERENCES

(1) Miller-Ihli N.J. *Slurry Sample Preparation for Simultaneous Multielement Graphite Furnace Atomic Absorption Spectrometry.* J. Anal. Atom. Spectrom. 1988; **3**: 73-81.

(2) Langmyr F.J., Wibetoe G. *Direct Analysis of Solids by Atomic Absorption Spectrophotometry.* Prog. Anal. Atom. Spectrosc. 1985; **8**: 193-256.

(3) Bendicho C., de Loos-Vollebregt T.C. *Solid Sampling in Electrothermal Atomic Absorption Spectrometry Using Commercial Atomizers - A Review.* J. Anal. Atom. Spectrom. 1991; **6**: 353-374.

(4) De Benzo Z.A., Velosa M., Ceccarelli C., De La Guardia M., and Salvador A. *Application of the Slurry Technique to Biological Materials: A Survey of Literature.* Fresenius Z. Anal. Chem. 1991; **339**: 235-239.

(5) Byrd E.D. *Determination of Trace Elements by Graphite Furnace Atomic Absorption Spectrophotometry with Solid and Slurry Sampling*, M.S. Thesis, Western Carolina University, Cullowhee, N.C., 1992.

(6) Wagley D., Schmiedel G., Mainka E., and Ache H.J. *Direct Determination of Some Essential and Toxic Elements in Milk and Milk Powder by Graphite Furnace Atomic Absorption Spectrometry.* Atom. Spectrosc., 1989; **10**: 106-111.

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