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Advances in ultrasonic slurry graphite furnace atomic absorption spectrometry *

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Summary. Ultrasonic slurry graphite furnace atomic absorption spectrometry is a useful technique for automated direct analysis of solids. The effectiveness of ultrasonic agitation for mixing samples is demonstrated. This analytical approach is evaluated to identify sources of imprecision. Strategies for optimizing slurry preparations are discussed, focusing on particle size, density, analyte partitioning, and sampling limitations. Finally, a teflon bead method is presented for grinding biological and botanical samples. An optimized general approach for ultrasonic slurry sampling is presented.

Introduction

Graphite furnace atomic absorption spectrometry (GFAAS) has proven to be a useful method for the direct analysis of solids as evidenced by a recent review by Bendicho and de Loos-Vollebregt [1] which cites more than 250 references. Advantages of solid sampling compared to conventional sample preparation procedures such as acid digestion include: 1) reduced sample preparation time; 2) decreased chance of analyte loss due to volatilization prior to analysis; 3) reduced loss of analyte related to retention by an insoluble residue; 4) reduced possibility of sample contamination; 5) increased sensitivity; 6) avoids use of hazardous acids; 7) facilitates selective analysis of microamounts of solid. GFAAS does not suffer from particle size effects like nebulization techniques do. Although solids have variable particle sizes suggesting possible problems with variable atomization efficiencies, the use of integrated absorbances with GFAAS which offers longer residence times, leads to accurate determinations of trace metals in solids. One of the problems with direct solid sampling which is most commonly reported in the literature relates to difficulty with automated sample introduction and poor precision with manual manipulation.

Slurry sampling has been identified as being an ideal approach to solid sampling which combines the benefits of solid and liquid sampling [2]. Solid material can be used to prepare a slurry or suspension and conventional liquid sampling devices can be used to introduce solid material into the furnace for analysis avoiding the difficulties experienced with direct solids analysis. In 1988 [3] the concept of manual ultrasonic mixing of slurries was introduced and in 1989 [4] an automated ultrasonic mixing accessory for slurry GFAAS was described. Perkin-Elmer Corp. developed the USS-100 Ultrasonic Slurry Sampler based on this technology [5, 6] and several successful applications have been reported in the literature using this approach [3, 7–11]. Accurate results can typically be obtained using as little as 1–5 mg of finely ground (< 500 μm) sample suspended in 1 ml of dilute acid or water which contains 0.005% Triton X-100 (Rohm and Haas, registered trademark for octyl phenoxypolyethoxyethanol, Sigma Chemicals). Analyses require the use of modern furnace technology including platform atomization and accurate background correction such as Zeeman effect. Calibration against aqueous standards provides accurate results. This paper provides a systematic evaluation of ultrasonic slurry GFAAS looking at the effectiveness of ultrasonic agitation, evaluating method imprecision, and identifying factors important for optimizing slurry preparations.

Experimental

Instrumentation

Determinations were made on either a Zeeman 5100PC spectrophotometer (Perkin-Elmer Corp., Norwalk, CT, USA) or on a prototype simultaneous multielement atomic absorption spectrometer (SIMAAC). Both spectrometers were equipped with an autosampler and a USS-100 Ultrasonic Slurry Sampler (Perkin-Elmer Corp., Norwalk, CT, USA). Wavelength selection for single element determinations was dependent upon the expected analyte concentration in the slurry and alternate lines were employed when concentrations were too high for the resonance wavelength. In all instances, charring and atomization temperatures had to be optimized for different sample matrices since the presence of organic constituents in the slurry can affect the selection of the optimum temperature. Graphite furnace parameters for both multielement and representative single element determinations are shown in Table 1. Parameters for

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Table 1. GFAAS Parameters

Element	Multielement	Cu	Fe	Cr
Wavelength, nm	Various	324.8, 216.5	248.3, 346.6	357.9, 429.0
Source (current)	300 W Cermax	HCL (15 mA)	HCL (20 mA)	HCL (25 mA)
Furnace program (Temp °C, Ramp s, Hold s)				
Dry	170, 20, 30	180, 40, 40	180, 40, 40	180, 40, 40
Pyrolysis	500, 20, 20	1100, 20, 40	1200, 20, 40	1450, 20, 40
Cooldown	–	20, 1, 10	20, 1, 10	20, 1, 10
Atomize	2700, 0, 10	2300, 0, 8	2400, 0, 8	2400, 0, 8
Cleanout	2700, 1, 5	2700, 1, 5	2700, 1, 5	2700, 1, 5
Matrix modifier	–	–	0.06 mg $Mg(NO_3)_2$	0.06 mg $Mg(NO_3)_2$
Concentration of highest std. (ng/ml)	5,000	50, 500	100, 5000	100, 500

multielement determinations reflect compromise conditions and the rationale for their selection has been discussed in detail previously [3]. Platform atomization was used for all determinations and peak areas (integrated absorbances) were used for quantification. Because this method can tolerate particle sizes up to several hundred microns, it was desirable to modify the autosampler to use AWG22 Teflon capillary tubing (810 μm i.d.) [12]. This modification had no effect on the delivery volume. A 12-gauge needle was used as a sleeve to hold the capillary and attach it to the autosampler arm.

Reagents

Ultrapure reagents were used throughout. Nitric acid used to prepare slurries and calibration standards was sub-boiling distilled acid (NIST, Gaithersburg, MD, USA). Water used was 18-MΩ deionized distilled water (Millipore, Bedford, MA, USA). Triton X-100 was added to slurry preparations with a final concentration of 0.005% (v/v). Standards were prepared daily in 5% (v/v) HNO_3. Single element standards were prepared to cover the linear range using 3–4 standards. Multielement standards contained equal concentrations of Al, Ca, Cu, Cr, Fe, Mg, Mn, Mo, Ni, Pb, V, and Zn. Eight multielement standards were used to cover over three orders of magnitude of concentration (1.0, 5.0, 10.0, 50.0, 100, 500, 1000, and 5000 ng/ml).

Slurry preparation

Slurries were usually prepared directly in a teflon autosampler cup. Typically 1–50 mg of finely ground material was used. Microweighing was done on a Mettler M3 (Mettler, Hightstown, NJ, USA) electronic microbalance. Static was controlled using the Staticmaster ion source (NRD Inc., Grand Island, NY, USA). Slurries were prepared in either 18-MΩ water or 5% HNO_3. All slurry preparations contained 0.005% Triton X-100 surfactant which served as a wetting agent and assisted in particle dispersion. Larger volumes of slurry were prepared using polyethylene test tubes or bottles and vortex mixing [9] was used to ensure adequate agitation while withdrawing a 1 ml aliquot for analysis.

Results and discussion

The analytical usefulness of ultrasonic slurry GFAAS has been reported previously [3, 7–11]. This author's experience has shown that as many as 8 elements can be determined simultaneously using compromise conditions and multielement results reflect good accuracy (±8–12%) [3]. The purpose of this research was to report specific data related to the optimization of the ultrasonic slurry GFAAS approach as well as to report on the method variance. Specific information regarding slurry optimization is included and a method for grinding biological and botanical samples is also discussed.

Table 2. Effect of various ultrasonic power settings

Power (%)	Cu concentration determined (μg/g)	
	Estuarine sediment SRM1646[A]	Rock sample[B]
20	13.4 ± 0.7	1.08 ± 0.23
35	14.8 ± 0.3	1.34 ± 0.01
55	16.0 ± 0.4	1.77 ± 0.06
60	15.9 ± 0.2	2.01 ± 0.05
80	15.3 ± 0.9	2.39 ± 0.15
100	15.4 ± 0.3	2.46 ± 0.10

[A] 2.0 mg/1 ml
[B] 24 mg/1 ml
n = 5

Ultrasonic mixing conditions

The USS-100 utilizes a Sonics and Materials (Danbury, CT, USA) Model VC-40 ultrasonic unit equipped with a stepped titanium probe. Optimum operating conditions require that the power output be adjusted so that the slurry is being vigorously mixed with a rolling action. Care was taken to avoid significant loss due to spattering. Unfortunately, power output to the probe is not constant from unit to unit and tuning is subjective. As a result, it is necessary to optimize conditions with each unit. In this work, an evaluation was made in the 40 W mode of operation and various power settings were tested to see what effect varying power levels had on accuracy and precision. Table 2 contains copper data for NIST SRM1646 Estuarine Sediment as well as a rock sample. These materials were selected because they are relatively dense and particles tend to settle out quickly. The certified copper concentration for NIST SRM1646 is: 18 ± 3 μg/g. Review of these data suggests that there is a threshold above which adequate agitation is obtained resulting in accurate determinations. A power setting of 60%

Table 3. Effect of alternating power settings

Power setting (%)	Estuarine sediment SRM1646
	Cu concentration determined (μg/g)
80	15.6 ± 0.5
30	11.7 ± 0.9
80	15.7 ± 0.5
30	12.2 ± 0.7

n = 15

proved adequate for the sediment while 80% marked the threshold for the rock sample.

Another point of interest relates to how precisely power settings had to be calibrated to ensure reproducible results. NIST SRM1646 Estuarine Sediment was used to evaluate alternating 80% and 30% power settings (Table 3). At the 80% power setting, accurate results were obtained with precisions of 3–4% relative standard deviation (RSD). Because 80% power exceeded the 60% threshold, there was no problem with the reproducibility of results between repeat 80% settings. At 30% power, mixing was inadequate leading to low results. In addition, precision was poorer (6–8% RSD). This study led to the adoption of the 80% power setting for the balance of the work reported.

The length of time used for mixing was also evaluated. The desire is to have adequate mixing to ensure that a representative subsample is injected into the furnace for analysis. Materials of varying particle size and density were studied. Figure 1 contains data for Cu, Fe, and Cr in a wide range of materials. In general, a 15–25 s mixing time was adequate for all materials. When the analyte is easily extracted into the liquid phase, a short mixing time can be used. One might expect that less dense materials do not require lengthy mixing but that is not the case. Particles with a density less than 1 g/cm^3 tend to float and ultrasound is effective in wetting particles as well as dispersing solids and dislodging mechanically interlocked particles [13]. Ultrasonic agitation proved to be very effective in mixing dense materials such as the sediment, ensuring that particles had not settled in the bottom of the conical shaped autosampler cup. It is unclear whether or not the high energy ultrasound actually splits up larger particles but many materials appeared to be more flocculent after ultrasonic mixing. Except for this study, mixing times of 25 s were used for all analyses reported here.

Several analysts have looked at alternative means of mixing slurries. Vortex mixing was successfully used by several researchers but this approach in not easily automated [3, 9, 14]. More recently, we compared Ar mixing as described by Bendicho and de Loos-Vollebregt [15] with ultrasonic mixing. Slurries were prepared using 5 mg of NIST SRM1632a Coal which has a certified Cr content of 34.4 ± 1.5 μg/g. Ultrasonic mixing was used to analyze two slurry preparations with the following results: 25.3 ± 1.3 μg/g Cr (no Triton X-100) and 34.7 ± 1.8 μg/g Cr (with Triton X-100). Argon bubbling using a flow rate of 75–80 ml/min produced the following result: 23.8 ± 1.2 μg/g (with Triton X-100). Review of these data suggests that Triton X-100 is necessary, even with ultrasonic agitation, to avoid agglomeration of particles which makes pipetting difficult and leads

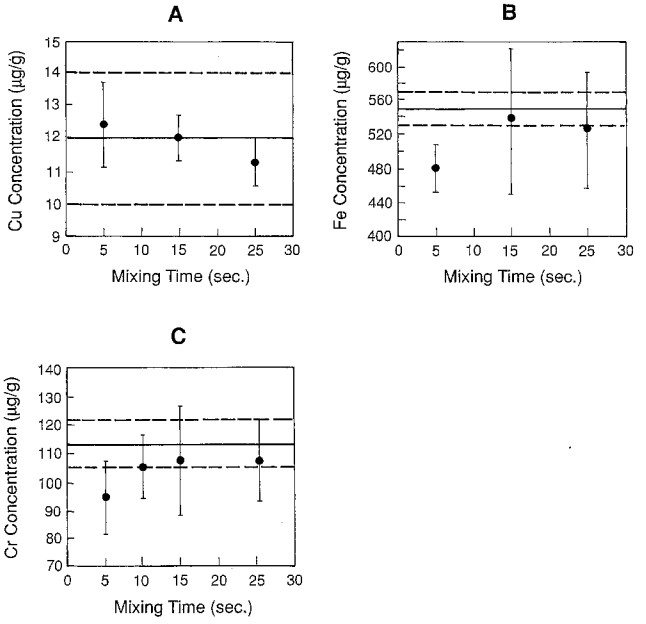

Fig. 1. Effect of ultrasonic mixing time on determined concentration of: **A**) Cu in Spinach SRM1570 (Certified Cu concentration: 12 ± 2 μg/g); **B**) Fe in Spinach SRM1570 (Certified Fe concentration: 550 ± 20 μg/g); **C**) Cr in PACS-1 Sediment (Certified Cr concentration: 113 ± 8 μg/g). The solid line denotes the mean reference concentrations and the dashed lines indicate the uncertainties

to inaccurate results. Argon mixing resulted in data which were 31% low compared to the mean NIST reference Cr concentration while ultrasonic mixing with Triton X-100 led to accurate results. The precision of both mixing methods was good but the argon mixing method apparently did not provide adequately vigorous agitation. A significant portion of the Cr is most likely associated with the more dense particles which may be up to 250 μm in diameter.

Characterization of method variance

Preliminary experiments were directed at identifying inherent sources of variability which were the result of the ultrasonic mixing approach. To ensure that interruption of the pump motors and the ultrasonic mixing itself did not provide a significant source of variability, aqueous standards were analyzed with and without ultrasonic mixing. The mean Cr concentrations determined analyzing 20 ng/ml and 50 ng/ml standards as samples with ten replicate measurements were as follows: 21.23 ± 0.15 ng/ml (0.70% RSD) mixed; 21.69 ± 0.24 ng/ml (1.10% RSD) unmixed; 52.89 ± 0.24 ng/ml (0.44% RSD) mixed; 55.96 ± 0.45 ng/ml (0.80% RSD) unmixed. Interestingly, the mixed standards provided slightly better precision than the unmixed standards. A statistical review of the data suggests that the RSD's for the standards, comparing mixed and unmixed, are not statistically significantly different ($\alpha = 0.05$). These data indicate that the slurry sample mixing and introduction system itself, does not provide a significant source of imprecision.

The precision of replicate measurements of aqueous standards and slurries were compared. The measurement precision due only to the slurry sampling ($\sigma^2_{\text{slurry sampling}}$) may be deconvoluted from the total slurry measurement precision (σ^2_{total}) by subtracting in quadrature the instrument pre-

Table 4. Measurement precisions for replicate analyses of a slurry

Slurry	Element	% Ext. liquid	Measurement precision, %			% of total variance		R
			Total RSD	Inst. RSD	Sl. Smpl. RSD	slurry sampling	Instrum.	
Sediment	Cu	60	2.44	1.14	2.16	78.2	21.8	3.6
Spinach	Cu	98	3.42	1.31	3.16	85.4	14.6	5.8
Coal	Cu	69	21.2	1.31	21.1	99.6	0.4	249
Cement	Cr	N.D.	3.16	0.70	3.08	95.0	5.0	19.0
Sediment	Cr	10	2.50	0.80	2.37	89.9	10.2	8.8
Spinach	Cr	74	18.9	0.82	18.8	99.8	0.2	499
Coal	Cr	2	3.60	0.80	3.51	95.1	4.9	19.4
Spinach	Fe	N.D.	18.8	0.68	18.7	99.8	0.2	500

cision ($\sigma^2_{\text{instrumental}}$) as follows: ($\sigma^2_{\text{slurry sampling}}$) = ($\sigma^2_{\text{total}}$) − ($\sigma^2_{\text{instrumental}}$). The total slurry measurement precision was characterized using replicate analyses of a slurry and the instrument precision was evaluated using replicate analyses of an aqueous standard of equivalent concentration. Table 4 contains measurement precision data for replicate analyses of single slurries prepared using 1.5 mg of a variety of materials. All final volumes were 1 ml. Measurement precision data for Cu, Cr, and Fe are presented. The difference between the slurry and instrumental measurement precisions is a function of the amount of analyte extracted into the liquid phase of the slurry, the degree of analyte homogeneity in the solid material, and the level of uncertainty associated with the slurry sampling. Another consideration is the particle size of the materials. Experience has shown that small particles are not necessary to obtain good accuracy and precision, in fact, many of the materials analyzed contain particles as large as 300 μm. Improved precision is, however, seen when working with a narrow range of particle diameters (e.g. 100 − 200 μm vs. 5 − 200 μm) [3]. Comparing the slurry sampling variance to the total variance, it is clear that for most slurries it exceeded 90%. Ratios of the slurry sampling variance and the instrumental variance, R, were computed: [$R = (\sigma^2_{\text{slurry sampling}})/(\sigma^2_{\text{instrumental}})$]. An F-test was used to determine at what level these two sources of variance were significantly different. All R values listed in Table 4 were significant ($\alpha = 0.05$, $n = 10$, $F > 3.0$) indicating that the slurry sampling variance was indeed significantly different than the instrumental variance.

The distribution of analyte in the slurry (liquid phase vs. solid phase) has been considered previously [3, 7, 9]. When no analyte is found in the liquid phase the limiting source of measurement variability from replicate aliquots of a single slurry will be related to the ultrasonic mixing coupled with the heterogeneity of the analyte in the insoluble fraction of the solid. When large percentages of analyte are extracted into the liquid phase, replicate aliquot precisions approach those of pure liquid digests. Looking at Table 4 it is clear that Cu is highly extracted into the liquid phase of each of the slurry preparations. The slurry sampling RSD is good for both the sediment and the spinach but is poorer for the coal. The 31% of Cu associated with the solid apparently is contributing to the poor precision since the instrumental variance is less than 1% of the total variance. This suggests that the coal is not very homogeneous for Cu at the mg level. Review of Cr data for spinach suggests that although a large amount of the Cr is extracted into the liquid phase, this material is also not very homogeneous at the mg level. A review of the sediment and coal slurries where Cr is not highly extracted into the liquid phase, show that both have RSD's in the 2 − 4% range. Because only 2% of the Cr was extracted into the liquid phase of the coal slurry, the 3.5% RSD respresents the precision obtainable at approximately the 30 μg level (2% of 1.5 mg). This highlights the usefulness of this technique for homogeneity characterization of sub-mg quantities of material.

Cu was determined in spinach slurries prepared using 2 mg of spinach in 1 ml of diluent. Five slurries were analyzed in triplicate on 2 different days. An analysis of variance (ANOVA) was done using the general linear model procedure of the Statistical Analysis System (SAS, Carey, NC). The ANOVA results provided information on the variance components. These were reviewed and 3.8% of the total variance was due to the readings while 96.2% was due to the weights (representing the different slurry preparations). The day-to-day variance was insignificant. Table 5 shows predicted relative standard errors (RSE's) based on the ANOVA results [16]. The RSE for the experiment completed was 2.08% (5 weights, 3 readings, 2 days). Note that the RSE is expected to be only 0.8% poorer if only 1 experiment is done (5 weights, 3 readings, 1 day). Clearly increasing the number of slurry preparations (weights) will have the greatest effect on an improved RSE. A table such as this can be an extremely useful tool in planning slurry experiments.

Optimizing slurry preparations

Several factors must be considered when optimizing slurry preparations. The most obvious concern is related to the amount of material being injected into the furnace for analysis. Computation of the mass of the solid material being placed into the furnace for analysis may be done as follows: $M_F = (M_S/V_S) \times V_F$ where M_F is the mass (in mg), M_S is the mass of sample used to prepare the slurry (in mg), V_S is the volume of the suspending fluid, and V_F is the volume of slurry added to the furnace [12]. For a slurry prepared using 5 mg of material in a volume of 1 ml, a 20 μl injection would put 100 μg of the solid into the furnace for analysis. The more material used to prepare a slurry with a fixed volume, the more representative the determined concentration will be of the analyte concentration in the original solid sample. This is particularly true if the analyte is extracted into the liquid phase of the slurry. If concentrations are too high to work in the optimum range for calibration, slurries may be diluted, alternate lines may be used, or in some instances, smaller volumes may be used.

Table 5. Predicted RSE for Cu, based on ANOVA

Reading	Weight 1	Weight 2	Weight 3	Weight 4	Weight 5	Weight 6	Weight 7	Weight 8	Weight 9	Weight 10
Day 1										
1	6.82495	4.82597	3.94038	3.41247	3.05221	2.78627	2.57959	2.41298	2.27498	2.15822
2	6.64331	4.69753	3.83552	3.32166	2.97098	2.71212	2.51094	2.34877	2.21444	2.10079
3	6.58166	4.65393	3.79992	3.29083	2.94341	2.68695	2.48763	2.32697	2.19389	2.08129
4	6.55061	4.63198	3.78200	3.27530	2.92952	2.67428	2.47590	2.31599	2.18354	2.07147
Day 2										
1	4.82597	3.41247	2.78627	2.41298	2.15824	1.97019	1.82404	1.70624	1.60866	1.52609
2	4.69753	3.32166	2.71212	2.34877	2.10080	1.91766	1.77550	1.66083	1.56584	1.48548
3	4.65393	3.29083	2.68695	2.32697	2.08130	1.89996	1.75902	1.65651	1.55131	1.47169
4	4.63198	3.27530	2.67428	2.31599	2.07148	1.89100	1.75072	1.63765	1.54399	1.46475
5	4.61876	3.26596	2.66664	2.30938	2.06557	1.88560	1.74573	1.63298	1.53959	1.46057
Day 3										
1	3.94038	2.78627	2.27498	1.97019	1.76219	1.60866	1.48933	1.39314	1.31346	1.24605
2	3.83552	2.71212	2.21444	1.91776	1.71530	1.56584	1.44969	1.35606	1.27851	1.21289
3	3.79992	2.68695	2.19389	1.89996	1.69938	1.55131	1.43624	1.34347	1.26664	1.20163
4	3.78200	2.67428	2.18354	1.89100	1.69136	1.54399	1.42946	1.33714	1.26067	1.19596
5	3.77120	2.66664	2.17730	1.88560	1.68653	1.53959	1.42538	1.33332	1.25707	1.19255

Table 6. Number of particles

Diameter (μm)	Particle volume, V_P (cm^3)	no. of particles/1 mg
25	8.18×10^{-9}	122,249
50	6.55×10^{-8}	15,267
100	5.24×10^{-7}	1,908
250	8.18×10^{-6}	122
500	6.55×10^{-5}	15

Table 7. Densities of several materials

Material	Density (g/cm^3)[A]
Bone	1.7–2.0
Clay	1.8–2.6
Coal (anthracite)	1.4–1.8
Coal (bituminous)	1.2–1.5
Glass	2.4–2.8
Paper	0.7–1.2
Oyster tissue SRM1566a	0.28
Coal SRM1632a	0.65
Bone meal SRM1486	0.81
Diet RM8431	1.09
Rice flour SRM1568	1.31
Bone ash SRM1400	1.95
Estuarine sediment SRM1646	2.47

[A] Densities for common materials are from reference [19] and densities for NIST reference materials (RM's) were experimentally determined.

A portion of this table was reprinted from reference [12] with permission

Holcombe and Majidi [17, 18] have characterized errors associated with slurry sampling considering the sample volume, the number of particles in the sample volume and the variation in the mass of the individual particles, concluding that errors can be minimized when working with small particles, concentrated slurries and narrow particle size distributions. When optimizing slurry preparations there are many factors which affect analytical performance including the homogeneity of the material, the distribution of analyte in the solid, the density of the material, the particle size, and the distribution of analyte in the slurry [3].

If the analyte is not homogeneously distributed in the solid, grinding samples to a very small particle size (< 10 μm) will increase the homogeneity of the slurry increasing the likelihood a representative mean concentration can be obtained. The density of the material and the particle size are also very important since both can be used to compute the number of particles in a particular mass of the solid material. Table 6 contains data pertaining to the total number of particles in a 1 mg sample of material with a density of 1 g/cm^3 for a variety of particle diameters. In all cases the assumption was made that particles are spherical. The number of particles may be computed as follows: $N_P = M_S/(D \times V_P)$ where N_P is the number of particles, D is the density and V_P is the volume of the particles. As the density of the material increases, the number of particles in a 1 mg portion will decrease linearly. As the mass of material increases, the number of particles will increase linearly. As the diameter of the particles double, the number of particles will decrease by a factor of 8.

The number of particles in a 20 μl injection may be calculated to ensure that a representative number are used for analysis. Clearly, as the number of particles decreases, sampling errors will become the limiting source of error. The mass of material needed to ensure that a 20 μl aliquot of a 1 ml slurry contains 50 particles, has been computed for a variety of particle size diameters and densities [13]. For materials with a density of 0.5 g/cm^3, 10 mg of material will provide a minimum of 50 particles/20 μl for particle diameters up to 250 μm. For a diameter of 500 μm, 82 mg of material is needed. For materials with a density of 2.5 g/cm^3, 50 mg of material will provide a minimum of 50 particles/20 μl aliquot for particle diameters up to 250 μm while 408 mg of material is needed for a diameter of 500 μm. Densities for several materials appear in Table 7. Experimen-

Table 8. Grinding study particle size data – broccoli. Cummulative % of particles smaller than specified diameter (% retained by specified sieve size)

	500	355	250	150	125	63	38	<38 μm
20 min	100	96.8	92.8	84.7	81.7	72.4	67.3	65.8
	(3.2)	(4.0)	(8.1)	(3.0)	(9.3)	(5.1)	(1.5)	(65.8)
40 min	100	99.7	98.7	93.8	92.4	89.5	83.9	81.8
	(0.3)	(1.0)	(4.9)	(1.4)	(2.9)	(5.6)	(2.1)	(81.8)
60 min	100	99.8	99.6	99.1	99.0	98.9	93.0	85.5
	(0.2)	(0.2)	(0.5)	(0.1)	(0.1)	(5.9)	(7.5)	(85.5)

tally determined average densities were obtained by filling a 0.5 ml autosampler cup with material and recording the mass of sample. Next, the dead volume was identified by adding surfactant to fill the cup and recording the volume added. Finally, the mass of sample per corrected volume (known cup volume – dead volume) was computed. This method was validated using materials of known density such as salt and sugar. Densities for many materials may be found in the CRC Handbook [19].

Material densities must also be considered when computing the volume of solid per unit volume of slurry in a liquid. The so-called volume/volume ratio can be so high that the slurry is too viscous for the autosampler to pipet. The volume/volume ratio can be computed as follows: $V/M/V_S = M_S/(D \times V_S)$ where V_M is the volume of solid, V_S is the volume of the suspending fluid, M_S is the mass of sample in grams and D is the density [13]. Practical experience has shown that when the ratio is ≤ 0.25 the slurry preparation can be pipetted easily and reproducibly. This would correspond to up to 100 mg of a material with a density of no less than 0.4 g/cm^3 prepared as a slurry with a 1.0 ml volume. This was evaluated using NIST SRM1566a Oyster Tissue which has an experimentally determined density of approximately 0.25 g/cm^3. Slurries prepared with 10, 25, 50, and 70 mg were pipetted easily while a slurry prepared using 100 mg of sample was too viscous.

Optimization of slurry preparations requires that each of the criteria discussed be considered in the preparation of the slurry. It is important that a representative sample be weighed out to prepare a homogeneous slurry, that the analyte concentration is in the working range of the calibration curve, that a representative number of particles be analyzed, and that the slurry is not too viscous to pipet. When slurries are diluted to facilitate easy pipetting or to reduce analyte concentrations in the furnace, care must be taken to ensure that a representative number of particles are injected into the furnace for analysis. Extraction of analyte into the liquid phase may lead to improved precision and allows a larger, more representative portion of material to contribute to the analytical determination. There are instances, however, when analyte extraction may be undesirable. An example is when homogeneity characterizations at the μg level are being performed.

Teflon bead grinding procedure

The benefit of reduced particle size to aid homogeneity has been discussed previously. In many instances, samples received for analysis are not finely ground homogeneous materials. As a result, it was necessary to identify a suitable grinding procedure. The relative merits of sample grinding were discussed previously and the zirconia bead method of Ebdon et al. [20] was evaluated [7]. Significant blanks were seen for Mn, Fe, Cu, Cr, Al, and Mg. More recently we evaluated the suitability of using teflon beads. Four different sizes were evaluated: ⅛″, ¼″, ⅜″, and ½″. The density of TFE is 2.15 g/cm^3. This approach is suitable for the preparation of many biological and botanical materials but would not be suitable for grinding very hard materials such as geological or metallurgical samples. The ½″ diameter beads were found to be the most effective. Experiments were done using 20 g of teflon beads (9 beads) with 3 g of sample. Sample and beads were placed in a 125 ml acid cleaned polyethylene bottle with 15 ml of either deionized distilled water or 5% sub-boiling distilled nitric acid. A wide range of sample materials were ground for 20, 40, and 60 minutes. Blanks were evaluated to ascertain contamination levels. Blanks for Cu, Mn, Fe, Cr, Co, Pb, V, and Mo were either not detectable or were less than 0.2 ng/ml and were not considered significant. Representative particle size data for ground broccoli samples are shown in Table 8. After 20 min 82% of the particles were <125 μm in diameter and this increased to 99% after 60 min of grinding. With the 20 min grinding time there were no particles >710 μm and only 3.2% were >500 μm. Based on these data and similar data for other materials, a 40 min grinding time was selected noting that this typically produced samples with 85–90% of the particles being <125 μm in diameter. Another point

Table 9. Slurry analytical data

Material	Element	Concentration, μg/g dry weight	
		Reference	Slurry
Diet	Mn	8.60 ± 0.31	8.60 ± 0.40
RM8431	Cu	3.36 ± 0.33	2.98 ± 0.40
Bread	Mn	5.59 ± 0.20	5.38 ± 0.49
Q87-BR-2788	Fe	43.7 ± 0.6	44.9 ± 3.9
	Cu	1.81 ± 0.08	2.12 ± 0.20
Tuna	Mn	0.35 ± 0.09	0.30 ± 0.03
Q87-TN-2785	Fe	29.9 ± 1.6	28.4 ± 2.7
	Cu	0.99 ± 0.07	0.79 ± 0.02
Cottage cheese	Mn	0.37 ± 0.03	0.36 ± 0.04
	Fe	2.94 ± 0.20	3.53 ± 0.60
	Cu	0.94 ± 0.10	0.88 ± 0.03

Table 10. Recommended procedure for ultrasonic slurry GFAAS determinations

1. *Grind the sample to produce a powder*
   - particle sizes up to 300 – 500 μm may be acceptable
   - grinding techniques include: mortar grinding, teflon beads and polyethylene bottles (biological/botanical samples); grinding, pulverizing, planetary, centrifugal or jar mills; cryogenic grinding
   - minimize contamination (avoid stainless steel)
   - do not sieve samples
2. *Plan to optimize slurry preparations*
   - prepare slurries which have analyte concentrations which are appropriate for the analyte line selected
   - factors of interest include: homogeneity of solid, distribution of analyte in the solid, density, particle size, and analyte partitioning in the slurry.
   - if analyte distribution is heterogeneous in the solid, strive for very small (< 10 μm) particles
   - compute the minimum mass required for analysis based on particle size and density (see Table 1)
   - compute the "volume/volume" ratio (volume of solid/volume of diluent) to ensure the ratio is ≤ 0.25
3. *Prepare slurries for analysis*
   - microweighing should be done on an electronic microbalance
   - 1 – 50 mg of ground material may be weighed directly into a teflon autosampler cup
   - 1.0 ml of diluent is added (5% sub-boiling distilled HNO_3 containing 0.004% Triton X-100)
   - slurries may be prepared using larger masses and/or volumes
4. *Analytical conditions*
   - wavelength selection will depend on analyte concentrations
   - less sensitive non-resonance lines may be useful
   - GFAAS conditions should be systematically optimized (e.g. char and atomization temperature studies)
   - STPF conditions should be used
   - quantitation is accomplished using aqueous standards using peak area measurements
   - the use of a matrix modifier and a char step may not be necessary
5. *Ultrasonic slurry mixing*
   - power output to ultrasonic probe should be adjusted to provide good mixing (typically 40 – 80%)
   - mix time 20 – 25 s
6. *Number of determinations*
   - typically 5 readings of each of 5 slurry preparations is adequate when analyzing an unknown sample
   - data should be reviewed to see if determined concentrations suggest a dependence on sample weight or sample heterogeneity

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is that grinding is not a time consuming process since bottles are placed on a wrist action shaker which operates unattended. Ground samples were filtered through a coarse mesh polyethylene screen to separate out teflon beads and were diluted to a final volume of 25 – 50 ml prior to analysis.

Three food samples (bread, tuna, and cottage cheese) as well as NIST RM8431 Diet were ground using this procedure and analyzed by slurry GFAAS. Data are presented in Table 9. In general, ultrasonic slurry data agree favorably with reference concentrations. The reference concentrations for the food materials were obtained by conventional acid digestion with detection by flame AAS. In general slurry precisions were somewhat poorer but this is expected since much smaller quantities of material were used to prepare the slurries (typically a few mg).

Conclusions

Ultrasonic slurry GFAAS is a powerful technique for the direct analysis of solids and can be used for rapid semi-quantitative screening or for high accuracy quantitative determinations. It is clear that some samples may have to be ground prior to analysis. Care must be taken to avoid contamination. The teflon bead grinding method described is suitable for biological and botanical materials. It is important to consider the statistical limitations of the technique when working with small numbers of particles. Extraction of analyte into the liquid phase can provide improved precision and is facilitated by the use of dilute acid as well as the use of ultrasonic agitation. Good precision may also be obtained when very little analyte is extracted into the liquid phase making the technique a powerful tool for homogeneity characterizations of materials. A particularly important consideration of ultrasonic slurry GFAAS is that method development and optimization can be based on conventional liquid sample protocols and often only limited changes are needed to facilitate the direct introduction of solids. Platform atomization, good background correction, and quantification using integrated absorbance measurements are essential for accurate determinations using aqueous calibration standards. A recently prepared outline based on the research presented here, summarizes a procedure for optimizing ultrasonic slurry GFAAS determinations and is presented in Table 10 [13].

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References

1. Bendicho C, de Loos-Vollebregt MTC (1991) J Anal Atom Spectrom 6:353

2. Stephen SC, Littlejohn D, Ottaway JM (1985) Analyst 110:573
3. Miller-Ihli NJ (1988) J Anal At Spectrom 3:73
4. Miller-Ihli NJ (1989) J Anal At Spectrom 4:295
5 Miller-Ihli NJ (1990) US Patent 4,930,898 (awarded June 5)
6. Carnrick GR, Daley G, Fotinopoulos A (1989) At Spectrosc 6:170
7. Miller-Ihli NJ (1990) Fresenius J Anal Chem 337:271
8. Jordan P, Ives J, Carnrick GR, Slavin W (1989) At Spectrosc 10:165
9. Epstein MS, Carnrick GR, Slavin W, Miller-Ihli NJ (1989) Anal Chem 61:1414
10. Bradshaw D, Slavin W (1989) Spectrochim Acta 44B:1245
11. Slavin W, Miller-Ihli NJ, Carnrick GR (1990) Am Lab 10:80
12. Miller-Ihli NJ (1992) At Spectrosc 1:1
13. Ultrasonics, Encyclopedia of Chemical Technology, 3rd edn, vol 23. Wiley, New York, 1983
14. Hinds MW, Jackson KW (1991) At Spectrosc 12:109
15. Bendicho C, de Loos-Vollebregt MTC (1990) Spectrochim Acta 45B:695
16. Douglas L (1992) USDA Statistical Services, private communication
17. Holcombe JA, Majidi V (1989) J Anal At Spectrom 4:423
18. Majidi V, Holcombe JA (1990) Spectrochim Acta 45B:753
19. CRC Handbook of chemistry and physics, 67th edn (1987)
20. Ebdon L, Fisher AS, Parry HGM, Brown AA (1990) J Anal At Spectrom 5:321