

# Use of the Hildebrand Grid Nebulizer for Inductively Coupled Plasma Atomic Emission Spectrometric Analysis of Foodware Leach Solutions and Rodent Soft Tissues and Femurs

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The Hildebrand grid nebulizer (HGN) was used for the inductively coupled plasma atomic emission spectrometric determination of major, minor and trace elements in perchloric acid digests of rodent femurs, sulphuric acid digests of rodent soft tissues and in solutions leached from foodware using acetic acid. The HGN performed well when the signal-to-background ratio was optimized for each acid solution by adjusting the injector gas flow, solution uptake rate and observation height. Three problems were overcome while using the HGN: (i) nebulizer wash-out time was reduced by rinsing at high uptake rate with the solution to be analysed; (ii) clogging of the injector tip of the torch during femur analysis was minimized by extensive rinsing; and (iii) errors due to the suppression of the Cu, Fe, Mn and Zn signal intensities by matrix elements Ca and P in femur digests were eliminated by calibrating the spectrometer with matched matrix standard solutions. Overall, the precision of analysis for the leach and tissue solutions analysed in this study ranged from 0.5 to 2.9% relative standard deviation.

**Keywords:** *Inductively coupled argon plasma atomic emission spectrometry; grid nebulizer; wash-out time; matrix effect; bone and biological tissue analysis; leach solution analysis*

The US Food and Drug Administration routinely uses inductively coupled argon plasma atomic emission spectrometry (ICP-AES) to analyse foodware leach solutions and rodent tissues and femurs. Leach solutions consist of 4% v/v acetic acid that has been in contact with foodware for 24 h at room temperature.<sup>1</sup> Rodent soft tissues are digested with a mixture of boiling nitric, perchloric and sulphuric acids until all the perchloric and nitric acid has been driven off and only sulphuric acid remains in the digest flask.<sup>2</sup> Whole rodent femurs are digested in a mixture of boiling nitric and perchloric acids until the reaction is complete and white fumes of perchloric acid are visible in the flask. All tissue digests are diluted with de-ionized water so that final solutions are 10% v/v in sulphuric or perchloric acid.<sup>2</sup> The cross-flow nebulizer (Perkin-Elmer Model N058-0358) designed for use with the spectrometer used in the present study performed poorly for these analyses. The solution capillary became clogged and required replacement at least twice per day during the analysis of femur digests containing high levels of Ca and P and moderate levels of K. After 2–3 d of nebulizer use, the solution began to leak through the space between the capillaries and nebulizer body and resulted in poor precision. Similar observations have been reported by others.<sup>3,4</sup>

Use of the Hildebrand dual grid nebulizer (HGN) was investigated in order to eliminate these problems. This nebulizer, which was designed for use with solutions containing high concentrations of dissolved solids, is constructed from high density polyethylene and platinum and offers more resistance to acid than the cross-flow nebulizer manufactured for the spectrometer used in this study. Solutions are pumped over a platinum grid located in front of a sapphire gas orifice through which argon flows. The second grid is mounted in an adjustable, threaded end cap, positioned downstream in the argon flow. The design of the nebulizer<sup>5,6</sup> and the characteristics of the aerosol it produces from de-ionized water<sup>7</sup> have been described by other workers. This paper presents the results of quantitative analyses using the HGN to analyse rodent bones and soft tissues, leach solutions and quality control (QC) solutions. The problems of long wash-out time and suppression of trace element intensity by high levels of Ca

and P are addressed. The optimization of the injector gas flow, solution uptake rate and observation height is also discussed.

## Experimental

### Instrumentation and Reagents

All experiments were performed on a sequential spectrometer equipped with an autosampler. Instrument specifications and optimized operating conditions for the plasma are given in Table 1. Analytical wavelengths and experimental parameters for the spectrometer are given in Table 2.

Single-element stock standard solutions, 1000 or 10000  $\mu\text{g ml}^{-1}$ , [Johnson Matthey AESAR Group, Seabrook, NH, USA, and National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899, USA, respectively] were used to prepare all working standards and QC solutions. All dilutions, designated v/v, were accomplished using calibrated pipettes and flasks. Analytical-reagent grade glacial acetic acid, diluted to 4% v/v, was used for acetic acid standards. Extra high-purity, concentrated perchloric and sulphuric acids ('double distilled' label, GFS Chemical, Columbus, OH, USA) were diluted to 10% v/v in order to obtain working standard solutions for tissue digests. Analytical-reagent grade phosphoric acid, calcium carbonate, sodium carbonate, potassium carbonate and magnesium sulphate were used to prepare simulated solutions of digested femurs and matched matrix standards. High purity concentrated nitric, perchloric and sulphuric acids ('redistilled' label, GFS Chemical) were used to digest rodent tissues, femurs and the NIST standard reference material (SRM 1577a, Bovine Liver). De-ionized water ( $\geq 18 \text{ M}\Omega$ ) was used in all preparations.

Concentrations of digests and QC solutions were calculated from emission intensity via the spectrometer software by comparison with the calibration standards. The spectrometer was standardized using two-point calibration (a blank and one standard) for analyses. The blank and standard solution contained 4% v/v acetic, 10% v/v sulphuric and 10% v/v perchloric acids for leach solutions, tissue digests and femur digests, respectively. The leach solution standard contained 1  $\mu\text{g ml}^{-1}$  of Cd and Mn and 10.0  $\mu\text{g ml}^{-1}$  of Pb. The tissue

**Table 1** Instrumentation and optimized operating conditions

Spectrometer	Perkin-Elmer Plasma 2 spectrometer (Norwalk, CT, USA). Two 1 m Ebert scanning monochromators capable of 0.009 and 0.018 nm resolution (monochromators A and B, respectively), operated at 4.0–6.7 Pa vacuum pressure
Radiofrequency generator	27.12 MHz R.f. generator with automatic tuning
Torch	Demountable (PE Model Type 1). Quartz injector tube, 1.46 mm i.d. (PE part No. 0047–3292), was modified to connect with ball joint on spray chamber and held tightly in place by a PTFE insert in the torch assembly
Spray chamber	Glass, double-pass (Scott type) without water cooling
Nebulizer	Hildebrand grid nebulizer (Leeman Labs, Lowell, MA, USA). The HGN adapter drain was sealed by attaching a short piece of tubing that was crimped closed. Waste solution was drained at a port located at the opposite end of the spray chamber. Injector gas flow was controlled by a thermostated mass flow controller. Argon gas flows were checked with a mass flow controller (Model 8200/8102-1433-FC, Matheson, Secaucus, NJ, USA) and a wet test meter (Model 63115, Precision Scientific, Chicago, IL, USA).
Solution delivery	12 Roller peristaltic pump, with standard poly(vinyl chloride) tubing, 0.76 mm (0.030 in) i.d., and tubing tension adjustment

*Optimized operating conditions—*

Forward power	1.1 kW
Observation height	12 mm
Solution uptake rate	1.0 ml min <sup>-1</sup>
Argon gas flow rate:	
Outer	15 l min <sup>-1</sup>
Intermediate	1 l min <sup>-1</sup>
Injector (4% v/v acetic acid)	0.70 l min <sup>-1</sup>
(10% v/v perchloric acid)	0.75 l min <sup>-1</sup>
(10% v/v sulphuric acid)	0.83 l min <sup>-1</sup>

digest standard contained 1 µg ml<sup>-1</sup> of Cu, Fe, Mn and Zn, 10 µg ml<sup>-1</sup> of Ca and Mg, and 25 µg ml<sup>-1</sup> of P. The standard used for femur digests contained 1 µg ml<sup>-1</sup> of Cu, Fe, Mn and Zn, 20 µg ml<sup>-1</sup> of Na and K, 2450 µg ml<sup>-1</sup> of Ca and 1225 µg ml<sup>-1</sup> of P.

**Procedure for Instrument Optimization**

Pump tension and nebulizer end cap position were adjusted before the HGN was installed on the spray chamber by setting the solution uptake rate and injector gas flow rate to 1.0 ml min<sup>-1</sup> and 0.8 l min<sup>-1</sup>, respectively, aspirating water and visually observing the aerosol formed. The end cap was positioned with respect to the nebulizer body so that a V-patterned aerosol, uniform over time, was formed. 'Spitting' occurred (large drops) when the cap was too far from the nebulizer body and 'skipping' occurred (gaps appeared at about 0.5–2 s intervals) when the cap was too close. The nebulizer was then attached to the spray chamber.

Combinations of injector gas flow and solution uptake rate that produced good (visually dense, non-skipping) aerosols were determined by aspirating the acid solution of interest and visually observing the aerosol formed in the spray chamber. Injector gas flow rates of 0.6–0.8, 0.6–0.8 and 0.8–0.9 l min<sup>-1</sup> were found for 4% v/v acetic, 10% v/v perchloric and 10% v/v sulphuric acids, respectively. Solution uptake rates of 0.8–1.0, 1.0 and 1.0 ml min<sup>-1</sup> were found for 4% v/v acetic, 10% v/v perchloric and 10% v/v sulphuric acids, respectively.

**Table 2** Analytical wavelengths and experimental parameters for the spectrometer

Element	Wavelength/ nm	PMT*/V	Sampling time†/ms	Background correction/ nm
<i>Monochromator A (survey‡ and peak§ windows = 0.050 and 0.025 nm, respectively)—</i>				
Cd I	228.802	850	500	±0.020
Cu I	324.754	800	200	±0.020
Fe II	259.940	800	200	±0.020
Mn II	257.610	750	250	±0.020
Ni II	221.647	850	200	±0.020
P I	213.618	750	250	Off
Zn I	213.856	800	500	±0.020

*Monochromator B (survey and peak windows = 0.075 and 0.035 nm, respectively)—*

Ca II	393.366	500	200	Off
K I	766.490	650	250	Off
Mg II	279.806	600	100	Off
Na I	589.592	650	250	Off
Pb II	220.353	850	1000	0.030

\* Photomultiplier tube.

† Time used per grating step to generate survey and peak profile data.

‡ Total wavelength range over which the spectral profile is taken.

§ Width surrounding analytical line which is used for curve fitting of intensity measurement.

The signal-to-background ratio was determined for a representative element at 5–6 different observation heights (10–20 mm above the load coil) for each flow combination that produced a good aerosol. Analyte emission was obtained from a solution containing 1 µg ml<sup>-1</sup> of Mn in the acid of interest. Background emission was obtained from the appropriate concentration of the same acid. Emission data were generated using the monochromator parameters listed in Table 2 with the exception of background correction, which was 'turned off'. The signal-to-background ratio was calculated as follows:

$$S/B = (EM_s - EM_b)/EM_b$$

where  $EM_s$  is the emission due to the analyte and  $EM_b$  is the emission due to the background.

**Monitoring Analytical Performance**

The spectrometer was calibrated with standard solutions once every 40–60 min in order to compensate for instrumental drift. Quality control solutions were analysed and the results were used to calculate precision because the volume of leach and tissue solution available for analysis was limited. The QC solutions contained acid concentrations equal to, and element levels similar to the unknown solutions. The QC solutions were analysed immediately after calibration of the instrument (before the analysis of leach, tissue or femur digests) and periodically during leach, tissue or femur analysis (QC solution in every sixth and eleventh tube following leach, tissue and femur tubes). When QC results deviated more than ±5% from known levels, all results obtained before the unacceptable QC analysis were discarded and the solutions re-analysed. Over-all method performance for soft tissue analysis was monitored by digesting and analysing 26 portions of NIST SRM 1577a (Bovine Liver) at regular intervals during the study.

**Results and Discussion****Wash-out Time**

Long wash-out times for the HGN have been reported by other workers<sup>6,8</sup> who eliminated this problem with extra

rinsing. It was decided not to use an extended rinse time in the present study because the time required to eliminate carry-over, when the rinse solution was pumped at the analytical rate, more than doubled the analysis time compared with other cross-flow nebulizers (Perkin-Elmer Model N058-0358 and Thermo Jarrell Ash Model 90-790) used on this spectrometer. Increased analysis time is undesirable for the analysis of large numbers of samples. In this study, wash-out time was reduced to an acceptably short time by rinsing the nebulizer and spray chamber with the solution to be analysed for 45 s at 4 ml min<sup>-1</sup>. Wash-out was considered adequate when a blank analysed immediately after an undiluted femur digest gave emissions of  $\leq 3 \times$  standard deviation (SD) of emissions obtained from a blank analysed before the undiluted femur digest.

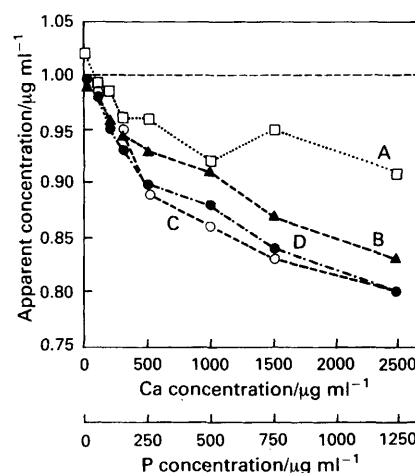
Varnes<sup>8</sup> reported decreased sensitivity in aqueous solutions when high pump rates were used for the HGN. During analysis of leach and tissue solutions, the high solution uptake rate required to rinse adequately in an acceptable time period also depressed trace element intensities. Intensities measured immediately after rinsing ( $t = 0$ ) were about 4% less than intensities measured after the aerosol had stabilized ( $t \geq 3$  min). In order to save time and reduce the volume of solution consumed, sequential measurements were initially taken 15 s after the uptake rate was resumed, *i.e.*, before the aerosol had stabilized. In order to obtain acceptable analytical precision, however, it was necessary to reproduce precisely (*i*) the rinse time; (*ii*) the solution uptake rate during rinsing; and (*iii*) the time after resuming the analytical uptake rate and before emission intensities were taken. An autosampler and a computer-controlled pump were used in this study to meet these requirements.

### Clogging of the Torch Injector Tip

Analysis of femur digests presented two problems not encountered in the analysis of soft tissue digests and acetic acid leach solutions. For all elements determined, results showing negative error were found for QC solutions analysed immediately after femur digests. The longer the femur digests were nebulized, the lower were the QC results. Visual inspection showed that clogging of the nebulizer did not occur but a white residue was deposited on the injector tip of the torch when low results were obtained. Other researchers have reported clogging of the injector tip,<sup>6,7</sup> which was reversed by rinsing with dilute nitric acid.<sup>6</sup> In the present work, it was necessary to rinse with 10% perchloric acid because changing solvents (from perchloric acid to nitric acid and back to perchloric acid again) adversely affected precision because of the accompanying change in solvent vapour pressure in the spray chamber. The design of the spray chamber drain on the ICP used in this study requires that the level of liquid in the drain tube be approximately 2.5 cm below the spray chamber and that the contents of the drain tube be changed every time a new solvent is introduced.

### Suppression of Trace Element Intensity

The second problem encountered in femur analysis was suppression of trace element intensities by high levels of Ca and P. When Fe and Zn were determined by calibrating the spectrometer with standard solutions containing 10  $\mu\text{g ml}^{-1}$  of Ca and 50  $\mu\text{g ml}^{-1}$  of P, the results were 83 and 77%, respectively, of the levels established for a laboratory control material (rabbit femur<sup>9</sup>). However, when analysed by the method of standard additions, levels found in the control material digest were 97 and 98%, respectively, of the established levels. The analysis of simulated femur solutions, containing 1  $\mu\text{g ml}^{-1}$  of Cu, Fe, Mn and Zn and increasing concentrations of Ca and P, confirmed that trace metal intensities were suppressed by up to 10% for Cu and 20% for Fe, Mn and Zn by the matrix elements (Fig. 1). When femur



**Fig. 1** Effect of Ca and P concentration on the results for A, Cu; B, Fe; C, Mn; and D, Zn. Analytical solutions contained 1  $\mu\text{g ml}^{-1}$  of Cu, Fe, Mn and Zn and increasing concentrations of Ca and P in 10% v/v perchloric acid. The spectrometer was standardized with solutions containing 10  $\mu\text{g ml}^{-1}$  of Ca and Mg, 50  $\mu\text{g ml}^{-1}$  of P, and 1  $\mu\text{g ml}^{-1}$  of Cu, Fe, Mn and Zn in 10% v/v perchloric acid

**Table 3** Analysis of QC solutions (containing 4% acetic acid and known concentrations of elements) and a typical leach solution (containing 4% acetic acid used to leach foodware)

Parameter	Element/ $\mu\text{g ml}^{-1}$		
	Pb	Cd	Mn
<i>QC solution analysed before analysis of leach solutions—</i>			
Actual	10.0	1.00	1.00
Mean ( $n = 30$ )	9.81	0.998	0.987
SD	0.116	0.00536	0.00658
RSD (%)	1.2	0.5	0.7
Outliers*	0	0	0
<i>QC solution analysed periodically during analysis of leach solutions—</i>			
Actual	10.0	1.00	NA†
Mean ( $n = 5$ )	10.03	1.00	NA
SD	0.089	0.012	NA
RSD (%)	0.9	1.1	NA
Outliers*	0	0	NA
<i>Leach solution—</i>			
Found ( $n = 1$ )	14.5	<LOQ‡	NA

\* Outliers = number of results which deviated more than  $\pm 5\%$  from the actual level.

† NA indicates solution not analysed for this element.

‡ <LOQ indicates not found above the limit of quantification which equals 0.01  $\mu\text{g ml}^{-1}$  ( $10 \times$  SD of the blank) for Cd.

digests were analysed by calibrating the instrument with standards containing 2500 and 1250  $\mu\text{g ml}^{-1}$  of Ca and P, respectively, the results were in 100% agreement with results obtained using the method of standard additions. These levels were chosen because a typical femur digest may contain about 2000–2500  $\mu\text{g ml}^{-1}$  of Ca and 1000–1250  $\mu\text{g ml}^{-1}$  of P. Matched matrix standard solutions were used for routine analyses because the method of standard additions is too time consuming for the analysis of large numbers of solutions and is not feasible for small volumes of digest such as those produced in animal experiments. Suppression of trace element emission by similar levels of Ca has been reported by Thompson and Ramsey for the analysis of geological materials.<sup>10</sup>

### Analytical Performance

Summaries of results obtained while monitoring analytical performance are presented in Tables 3–5 for acetic, sulphuric and perchloric acid solutions, respectively. The data in Tables



**Table 4** Analysis of QC solutions (containing 10% v/v sulphuric acid and known concentrations of elements) and digests of NIST SRM 1577a Bovine Liver (in 10% v/v sulphuric acid)

Parameter	Element/ $\mu\text{g ml}^{-1}$						
	Cu	Fe	Mn	Zn	Ca	Mg	P
<i>QC solution analysed before analysis of tissue digests—</i>							
Actual	1.00	10.0	1.00	1.00	5.00	5.00	25.0
Mean ( $n = 32$ )	0.998	9.87	0.982	0.986	4.97	4.99	24.9
SD	0.008	0.088	0.012	0.011	0.056	0.05	0.292
RSD (%)	0.8	0.9	1.2	1.1	1.1	1.0	1.2
Outliers*	0	0	0	0	0	0	0
<i>QC solution analysed periodically during analysis of tissue digests—</i>							
Actual	1.00	10.0	1.00	1.00	5.00	5.00	25.0
Mean ( $n = 26$ )	0.995	9.94	0.992	0.990	4.97	4.99	24.8
SD	0.018	0.106	0.01	0.017	0.15	0.061	0.527
RSD (%)	1.8	1.1	1.0	1.7	2.9	1.2	2.1
Outliers*	0	0	0	1	1	0	2
<i>NIST SRM 1577a digests†—</i>							
Mean ( $n' = 26$ ) $\ddagger\mu\text{g g}^{-1}$	147	180	9.7	118	128	595	11300
RSD (%)	8.8	11.0	8.7	8.6	8.3	8.4	8.8
Percentage of certified value	93	93	98	96	107	99	102

\* Outliers = number of results which deviated more than  $\pm 5\%$  from the actual level.† Dilution factor for SRM digests is approximately  $0.01 \text{ g ml}^{-1}$ . $\ddagger n'$  = Number of individual portions digested. Each digest was analysed once.**Table 5** Analysis of QC solutions (containing 10% v/v perchloric acid, known concentrations of trace elements,  $2450 \mu\text{g ml}^{-1}$  of Ca and  $1225 \mu\text{g ml}^{-1}$  of P) and a typical femur digest (in 10% v/v perchloric acid)

Parameter	Element/ $\mu\text{g ml}^{-1}$					
	Cu	Fe	Mn	Zn	Na	K
<i>QC solution analysed before analysis of femur digests—</i>						
Actual	1.00	1.00	1.00	1.00	10.0	10.0
Mean ( $n = 9$ )	1.01	0.997	1.00	1.01	10.0	9.80
SD	0.011	0.013	0.008	0.017	0.117	0.114
RSD (%)	1.1	1.3	0.8	1.7	1.2	1.2
Outliers*	0	0	0	0	0	0
<i>QC solution analysed periodically during analysis of femur digests—</i>						
Actual	1.00	1.00	1.00	1.00	25.0	25.0
Mean ( $n = 73$ )	0.992	0.974	0.993	0.996	24.6	24.9
SD	0.020	0.014	0.011	0.019	0.51	0.58
RSD (%)	2.0	1.5	1.1	1.9	2.1	2.3
Outliers*	2	3	0	0	4	3
<i>Femur digest†—</i>						
Found ( $n = 1$ ) $\mu\text{g g}^{-1}$	1.5	32	<LOQ $\ddagger$	156	4130	6130

\* Outliers = number of results which deviated more than  $\pm 5\%$  from the actual level.† Dilution factor for femur digests is approximately  $0.01 \text{ g ml}^{-1}$ . $\ddagger$  <LOQ indicates not found above the limit of quantification which equals  $1.0 \mu\text{g g}^{-1}$  ( $10 \times \text{SD of the blank}$ ) for Mn.

3–5 were collected during time periods ranging from 1 h to 10 d and provide an estimate of the over-all precision of analysis for the leach and tissue solutions analysed.

The precision obtained using the HGN was good for the solutions analysed in this study. Ranges of relative standard deviation (RSD) for QC solutions analysed before analysis of leach, tissue or femur solutions were 0.5–1.2% for acetic acid, 0.8–1.2% for sulphuric acid, and 0.8–1.7% for perchloric acid. The precisions of QC solutions, analysed after 5–10 tissue digests, were 1.0–2.9% RSD for QC solutions in 10% v/v sulphuric acid and 1.1–2.3% RSD for QC solutions containing high levels of Ca and P in 10% v/v perchloric acid. The over-all precision of the method for soft tissue analysis, calculated from results of 26 portions of SRM 1577a taken through the digestion procedure and analysed once, was 8.3–11% RSD.

The number of outliers (results deviating more than  $\pm 5\%$  from the actual level in the QC solution) indicates how seldom the analyst was required to re-analyse tissue and femur digests when using the HGN. When QC solutions were analysed periodically during the analysis of tissue and femur solutions,

approximately 16% of the results deviated more than  $\pm 5\%$  from the actual level (4 out of 26 for sulphuric acid and 12 out of 73 for perchloric acid). No outliers were obtained, however, when QC solutions were analysed before tissue or femur solutions were introduced. Outliers obtained during the analysis of tissue and femur digests may be due to trace levels of undigested organic material. The number of outliers obtained when QC solutions were analysed periodically during the analysis of leach solutions was the same as when QC solutions were analysed before the leach solutions because the compositions of the QC and leach solutions were not significantly different.

### Conclusions

The HGN provided good precision when injector gas flow and observation height were optimized for 4% v/v acetic acid, 10% perchloric acid and 10% v/v sulphuric acid. The greatest advantage in using the HGN, however, was that perchloric acid solutions of digested femur did not clog the nebulizer.

Although the problem of nebulizer clogging was eliminated by using the HGN, high salt content in femur digests clogged the injector tip of the torch. Extra rinsing, in addition to the rinsing required to eliminate carryover, was necessary in order to prevent blockage of the injector tip for these digests. The use of matched matrix standard solutions was essential to compensate for severe suppression of trace element intensity in femur digests. The major drawback in using the HGN was the large volume of solution required to eliminate carryover from the previous analysis. The wash-out time was shortened by rinsing with the solution at a high uptake rate, but precise timing of the rinse and analysis was necessary in order to obtain acceptable precision.

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