

Continuum Source Atomic Absorption Spectrometry in an Air-Acetylene Flame with Improved Detection Limits

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A continuum source atomic absorption spectrometer with flame atomization and photodiode array detection is described. High-resolution atomic absorption spectra spanning a spectral window of 9 nm are obtained using a 5-s integration period. As many as 11 elements can be detected in a single spectrum. The improved light-gathering power of the system results in detection limits similar to those observed with conventional line source systems at wavelengths as low as 223 nm. For example, detection limits of 2 ng/mL are observed for Cd (228 nm), Mn (279 nm), and Ag (328 nm). Linear dynamic ranges spanning 3 orders of magnitude are typical, with extended ranges up to 6 orders of magnitude possible by monitoring more than one atomic line for a single element.

INTRODUCTION

In conventional atomic absorption spectrometry (AAS), atomic line sources such as hollow cathode lamps are used in combination with a medium-resolution monochromator and a photomultiplier tube detector. One of the major disadvantages associated with conventional line source AAS is that only one element can be determined at a time: the replacement and realignment of single-element lamps can be time consuming and expensive, depending upon the number of lamps required. Although multielement hollow cathode lamps are available, they are not widely used due to their relatively low intensity, reduced sensitivity and high background noise compared to the single-element lamps.

Most of the attempts to make AAS a multielement technique have centered around the use of continuum sources such as the xenon arc lamp.¹⁻⁵ The growth of continuum source atomic absorption spectrometry (CSAAS) during the past 3 decades has produced numerous system designs, but only one has been extensively characterized and applied to a wide variety of real samples. This instrument called SIMAAC (simultaneous multielement atomic absorption with a continuum source) has been operational for the past 11 years.⁶⁻¹² The system consists of a 300-W xenon arc source,

a wavelength-modulated echelle polychromator, and a bank of photomultiplier tube detectors (one for each element to be determined). Despite the numerous publications using the instrument, no commercial instrument has been developed, largely as a result of the following disadvantages. SIMAAC detection limits are about 1 order of magnitude worse than typical line source AAS detection limits, especially at wavelengths below 280 nm. Furthermore, since the SIMAAC system was designed to be used primarily with a graphite furnace atomizer, the mandatory use of compromise furnace atomization conditions has been raised as a second objection from instrument manufacturers.

Multichannel detectors may offer significant improvements to the SIMAAC design. One system employing an echelle spectrometer and an image dissector has been evaluated for multielement determinations.^{13,14} Detection limits within a factor of 6 of conventional line source values were obtained for Ca, Cr, Cu, and Mn.¹³ The system is limited in two respects.¹⁴ The echelle grating limits the utility of the system in the ultraviolet region below 300 nm. Spectral order overlap complicates the total spectral coverage as well.

The image dissector recently has been replaced by a charge injection device (CID).¹⁵ In order to match the physical dimensions of the CID detector system, the echelle polychromator was modified to achieve a 3-fold image reduction at the exit focal plane. The resulting instrument was capable of continuously monitoring a 40-nm spectral window in the wavelength range 300-430 nm. The sensitivity of the new instrument was similar to that found with the image dissector system. While the system offered many advantages, detection limits as low as those observed with line source systems were not realized. Measurements were not possible at wavelengths below 280 nm where CSAAS systems are typically inferior to line source systems. Unfortunately, many of the strongest atomic absorption lines are found in this region.

The linear photodiode array (PDA) detector has been used previously in multielement line source AAS systems.^{16,17} The PDA also has been used in CSAAS systems in combination with an echelle monochromator and a pulsed xenon arc lamp.^{18,19} The detector employed with that system contained 256 pixels and covered a spectral window of approximately 0.6 nm. The PDA was centered around a single atomic absorption line, and pixel averaging was necessary to improve signal to noise ratios. Use of the photodiode array detector

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eliminated the need for the mechanical wavelength modulation process. Pulsing the xenon arc lamp led to increased intensity in the ultraviolet region. Signal to noise ratios measured with the new system were compared to those observed with the previously reported SIMAAC systems using photomultiplier tube detectors. Improvement factors on the order of 5.8–8.5 were reported for the five elements tested. To perform multielement analyses, the pulsed source system could incorporate a separate array for each atomic absorption line of interest. Since the ultimate goal of this SIMAAC system was to use the graphite furnace atomizer, short integration times (12.5–16.7 ms) were used in the reported study. Improved results using the flame atomizer would be expected if longer integration times were employed.

The linear PDA detector has been used in conjunction with a Perkin-Elmer Model 303 AAS system for monitoring matrix interferences associated with graphite furnace AAS.²¹ A similar detector has also been employed in the characterization of crude oils by their molecular and atomic spectral bands.²² The PDA had not been used as the primary detector in a multielement CSAAS without an echelle spectrometer until recently. In 1989 three papers were published describing such a CSAAS system in combination with flame, furnace, and inductively coupled plasma atomization.^{23–25} In all cases the instrumentation consisted of a 300-W xenon arc lamp, an atomizer, a Czerny-Turner high-resolution monochromator and the PDA. The high-resolution monochromator was operated in the fifth order to achieve a system resolution comparable to the width of a typical atomic absorption profile. A predispersing monochromator was placed prior to the high-resolution monochromator to prevent spectral order overlap. The detection limits reported for this system were 1–2 orders of magnitude worse than those reported for line source systems.

The problems associated with the PDA-CSAAS system mentioned above^{23–25} included inadequate resolution, low source intensity especially below 250 nm, and a limited spectral window covered by the detector (2.5 nm). Nevertheless, this system exhibits great potential in CSAAS applications, especially if improvements can be made toward increasing the measured intensity of the source radiation. This may be achieved by employing a more powerful source or by using longer signal integration periods. Improvements by these two means are impractical. The 300-W xenon lamp is the standard source in CSAAS, and the expense of a stronger source would not be justified by the limited improvements expected. Furthermore, integration periods longer than 5 s would result in impractical analysis times. Alternatively, in the work presented here, the measured source signal will be increased by improving the total light throughput of the optical system. The new CSAAS instrument will incorporate a monochromator with sufficient resolving power so that first-order diffraction can be used to match the spectral band-pass to the width of the atomic absorption profile. The limited wavelength coverage associated with the previous system will also be increased by using a longer PDA.

EXPERIMENTAL SECTION

Instrumentation. Figure 1 is a schematic diagram of the optical arrangement used in this work. The light source is a

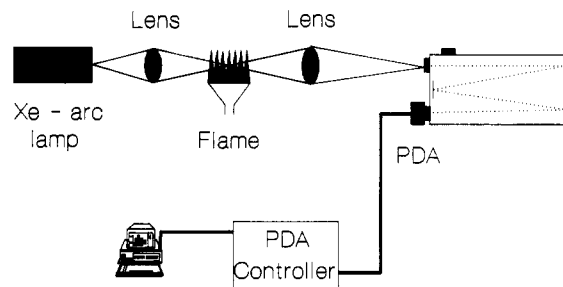


Figure 1. Schematic diagram of the continuum source atomic absorption spectrometer.

300-W xenon arc lamp (Cermax, ILC Technology, Sunnyvale, CA). The relative intensity of the Cermax lamp is generally 1 order of magnitude higher than the corresponding values for hollow cathode lamps.^{2,26} The spectral and noise characteristics of the lamp are well-known, and it has been recommended for use in CSAAS experiments.^{26,27} The collimated output from the lamp is focused through the center of the analytical flame produced by an air/acetylene nebulizer burner system (Perkin-Elmer) with a slot burner head.

The unabsorbed radiation exiting from the opposite end of the flame is focused directly onto the entrance slit of a high-resolution monochromator (McPherson Model 209, Acton, MA). The monochromator has a focal length of 1.33 m and it is equipped with a 3600 groove/mm holographic grating. This resulted in a solid angle of collection, Ω , of 0.006 sr ($F/\lambda = 11.6$) and a measured reciprocal linear dispersion in the range 0.15–0.20 nm/mm (depending on the analytical wavelength). The slit width and height are adjustable from 5 to 4000 μm and 0 to 20 mm, respectively, and the system has a total operating range between 185 and 650 nm with an optimum efficiency between 200 and 440 nm. Manual scanning is possible, and a motor-driven scan controller (McPherson Model 788) is attached to provide computer-interfacing capability for automation.

The photon flux at the exit focal plane of the monochromator is detected with a self-scanning photodiode array (Princeton Instruments Model PDA-2048, Trenton, NJ). The array is 5.0 cm wide, 2.5 mm high and incorporates 2048 photodiodes linearly aligned on 25- μm centers. The resolution of the PDA is given in the manufacturer's literature as 1–2 diodes. The spectral range of the detector is 180–1060 nm, and it is cooled to an operating temperature of -40°C . The PDA is operated with a high-speed 16-bit controller (P.I. Model ST-1000) with a 9-ms readout time (4 μs /diode). The controller is interfaced with a Zenith Model 386SX personal computer.

Monochromator entrance slit parameters are held constant for each analyte. The physical dimensions of the PDA theoretically restrict the slit width to 25 μm (the width of one photodiode) for the preservation of the system resolution. Higher slit widths result in lower absorbance signals due to radiation outside of the atomic absorption profile falling on the diode. Significant deviations from Beer's law are observed in this case. Smaller slit widths result in lower signal to noise ratios (S/N) due to reduced monochromator throughput. Both signal (S) and noise (N) were measured in absorbance units. Experimental variation of the slit widths from 10 to 60 μm , in 10- μm intervals, resulted in a maximum S/N at a slit width of 20 μm . The resulting spectral band-pass of the monochromator/PDA combination is on the order of the average atomic absorption profile half-width (0.003–0.005 nm). This resolution is comparable to that achieved by other systems evaluated for CSAAS measurements.²⁸ The slightly greater than 1 ratio of the spectral band-pass and the atomic absorption profile theoretically results in maximized absorbance readings while preserving linear Beer's law relationships.²⁹

Similarly, the entrance slit height is theoretically limited by the height of a single photodiode (2.5 mm). Slit heights were

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Table I. Optimum Detector Parameters for Single-Element CSAAS Analyses

element	wavelength (nm)	exposure (ms)	no. of spectra accumulated
Zn	213.856	1000	5
Bi	223.061	1000	5
Cd	228.802	750	7
Co	240.745	1000	5
Au	242.795	100	50
Pd	244.791	1000	5
Fe	248.327	750	7
Mn	279.482	1000	5
Pb	283.305	100	50
Mg	285.213	100	50
In	303.936	100	50
Cu	324.754	250	20
Ag	328.068	100	50
Ni	352.454	100	50
Cr	357.869	100	50

experimentally varied from 0 to 20 mm in 2-mm intervals. At slit heights higher than the 2.5 mm, part of the radiation passing through the monochromator does not fall on the diode array. As a result the S/N remains constant. At slit heights less than 2.5 mm, less light falls on each diode, resulting in a lower S/N. A constant slit height of 4 mm was chosen to ensure complete illumination of the PDA with minimal amounts of excess light (which could result in increased amounts of scattered radiation).

Other system parameters, such as flame and detector variables, were optimized for each of the 15 elements determined. In order to compensate for the low source intensity at wavelengths below 280 nm, higher PDA exposure times were used. Higher exposure times resulted in a higher measured source intensity and a lower noise level, leading to significant S/N improvements. Since different exposure times were used for different elements, a constant total integration period of 5 s was maintained by averaging (or accumulating) successive detector exposures. For example, in the case of Zn (213 nm) five spectra were accumulated, each with a 1000-ms exposure. Fifty successive spectra with 100-ms exposure times were accumulated for Ni (352 nm), resulting in an overall analysis time of 5 s. Six different exposure/accumulation combinations were employed. The lamp intensity and noise level at a particular wavelength dictated the best exposure/accumulation combination for a particular element (Table I). The use of higher exposure times was limited by the saturation level of the PDA, particularly at wavelengths higher than 320 nm. The high light levels observed in each case ensured that the detector was photon shot noise limited.

Flame conditions such as observation height, air/fuel ratio, and rate of solution intake were optimized individually for each element. Of these three parameters, the air/fuel ratio had the largest effect on the S/N ratio from element to element. Among the 15 elements determined, only Cr was found to have an air/fuel ratio drastically different from the rest of the elements (highly reducing yellow flame). In some cases, slight changes in the air/fuel ratio had a greater impact on the background noise due to interference arising from OH absorption bands. This was the case for Mg and Pb in the 285-nm range and In at 304 nm. Typical observation heights in the flame were about 5 mm above the slot burner head, and solution uptake rates were on the order of 10 mL/min.

Reagents. Aqueous stock solutions (1000 mg/L) were prepared for each of the 15 elements as previously described.³⁰ A range of standard solutions for calibration curves was prepared by serial dilution with distilled/deionized water. Standard solutions containing mixtures of the metals were used for multielement analyses.

Procedure. Absorbance spectra were obtained as follows. The proper wavelength for the element of interest was selected on the monochromator. A dark spectrum, *D*, was collected with the shutter on the entrance slit closed. The shutter was opened, and a spectrum of the incident source radiation, *I*₀, was obtained while deionized water was aspirated into the sample flame.

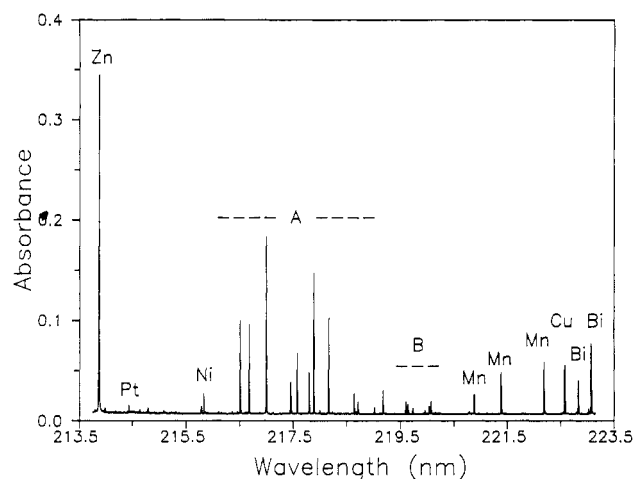


Figure 2. CSAAS spectrum of a multielement mixture in the region of the major absorption line for zinc. Each element is present at a concentration of 70 $\mu\text{g/mL}$. The data plotted in this spectrum represent all 2048 photodiode pixels on the detector array. Expanded views of the spectrum under regions A and B are given in Figures 3 and 4.

Finally, the sample spectrum, *I*, was obtained by the aspiration of a standard solution. The absorbance spectrum, *A*, was calculated using the computer software available with the PDA as follows:

$$A = \log \frac{(I_0 - D)}{(I - D)}$$

Background-corrected absorbance values were collected for each element as follows. Five consecutive absorbance spectra were calculated for each standard solution as stated above, each with a total integration time of 5 s (Table I). The observed full width at half-maximum (fwhm) for each atomic absorption line was equivalent to a maximum of 3 photodiodes. Uncorrected absorbance values were taken at the single diode with the highest signal. A background signal, taken as the average absorbance signal for 10 diodes neighboring the absorption line (5 diodes on each side), was subtracted from each value. The precision observed for the five consecutive signals obtained in this manner varied with analyte concentration. At concentrations very near the detection limit (within a factor of 5) the relative standard deviation was typically 9%. At concentrations 10 times higher than the LOD, a 5% RSD was typical; and at concentrations 100 times greater than the LOD, relative standard deviations less than 1% were observed.

RESULTS AND DISCUSSION

Absorption Spectra. Atomic absorption spectra collected with the photodiode array detector have been previously published in just a few cases.²¹⁻²⁵ Two of these works focused on simultaneous molecular and atomic absorption measurements, resulting in poor resolution of the atomic lines.^{21,22} The previous high-resolution spectra were confined to 2.5-nm spectral windows due to system restraints.²³⁻²⁵ Figures 2-4 demonstrate the capabilities of the current system. Figure 2 is an atomic absorption spectrum for a mixture of 11 metals each at a concentration of 70 $\mu\text{g/mL}$. Each element in the solution exhibits at least one absorption line within the 9-nm region covered by the PDA. Expanded views of the spectrum (Figures 3 and 4) demonstrate the noise levels commonly encountered at wavelengths below 220 nm. For example, the spectrum in Figure 4 has a peak to peak noise on the background of about 0.0002 absorbance units (au). This value is similar to that reported for typical line source systems³¹ using new hollow cathode lamps, pure sample solutions, and integration times of 3-10 s. Also, the resolving power of the

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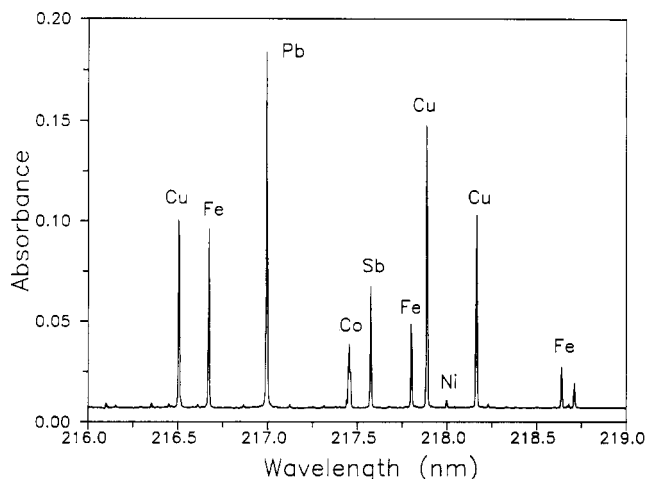


Figure 3. Expanded view of a multi-element CSAAS spectrum in the region of a major absorption line for lead. The wavelength region covered in this spectrum represents photodiode pixels 492–1145 on the detector.

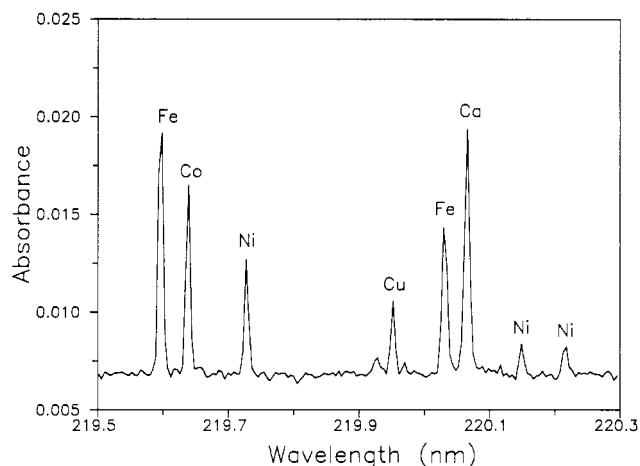


Figure 4. Expanded view of a multi-element CSAAS spectrum showing baseline resolution between the iron line at 220.04 nm and the calcium line at 220.07 nm. The wavelength region covered in this spectrum corresponds to photodiode pixels 1255–1429 on the detector.

system is clearly demonstrated by the complete baseline resolution of the iron line at 220.04 nm and the calcium line at 220.07 nm. The maxima of the two absorption peaks were separated by only 7 photodiodes on the PDA. The full width at half-maximum (fwhm) for each peak was measured as slightly less than 2 photodiodes (approximately 0.006 nm). Finally, the background correction capabilities of the instrument are clearly evident since the non-zero background absorbance can be easily subtracted from the measured peak height upon inspection.

Analytical Figures of Merit. Analytical figures of merit for 15 of the elements studied are given in Table II. The limits of detection (LOD) were calculated using the IUPAC definition.³² The LOD corresponds to the concentration of analyte producing an absorbance signal equal to 3 times the standard deviation in the blank signal. In each case, the LOD for the present system is approximately 1 order of magnitude lower than previously reported CSAAS detection limits using flame atomization.² This significant improvement may be attributed to the improved light-gathering capability of the present instrument compared to the echelle spectrometer. This results in part from a significantly larger slit height used with the present system. Furthermore, except for the case

Table II. Representative Analytical Figures of Merit Observed for CSAAS with Flame Atomization

element	wavelength (nm)	detection limit ^a (ng/mL)			linear dynamic range (decades)
		this work	SIMAAC ^b	line source ^c	
Ag	328.068	2	7	3	3.3
Au	242.795	10	200	20	3.2
Bi	223.061	30	300	30	3.2
Cd	228.802	2	30	1	3.0
Co	240.745	6	70	4	3.0
Cr	357.869	4	20	4	2.9
Cu	324.754	0.9	10	2	4.2
Fe	248.327	6	70	6	3.4
	370.925	2000			3.2
	371.994	10			4.0
	373.332	200			3.0
	374.336	6000			3.2
In	303.936	9		30	2.1
Mg	285.213	0.3	1	0.2	3.1
Mn	279.482	2	10	2	3.7
Ni	352.454	6	70	3	3.0
Pb	283.305	10	100	8	3.5
Pd	244.791	8	100	20	3.3
Zn	213.856	10	70	1	2.8

^a Calculated for a S/N of 3. ^b Taken from ref 2. ^c Taken from ref 31.

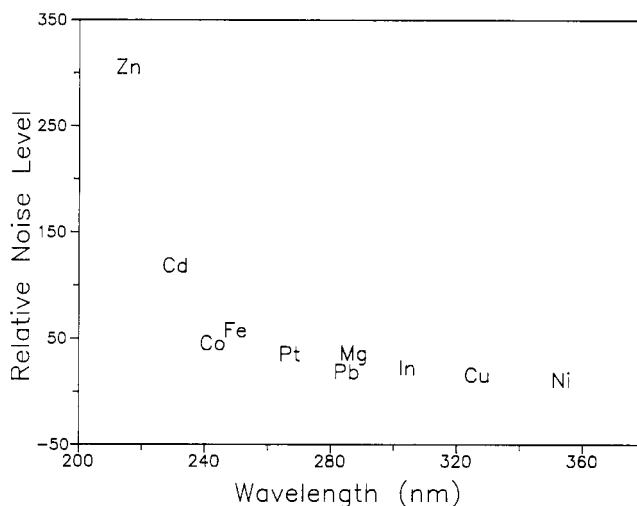


Figure 5. Diagram demonstrating the relationship between the noise level observed for a blank solution measured with the CSAAS system and the wavelength of absorption. The relative noise level is given in absorbance units multiplied by 10^6 . The noise was taken as the standard deviation in the absorbance signals measured for 10 adjacent diodes at the appropriate analytical wavelength.

of Zn at 213.86 nm, the present detection limits are on the same order of magnitude as those commonly observed with single-element hollow cathode lamp systems.³¹ The increased LOD for Zn (by a factor of 10) may be attributed to a general increase in the noise level of the system with decreasing wavelength (Figure 5). This increase in noise level arises from several sources. The output intensity of the xenon arc lamp decreases with decreasing wavelength, even though it remains more intense than the corresponding hollow cathode lamps.²⁶ For example, a reduction in source intensity by a factor of 10 has been documented between the Fe line at 248.327 nm and the Zn line at 213.856 nm.^{2,26} This trend is even more pronounced below 220 nm where the source intensity drops by a factor of 3 between the Pb line at 217.000 nm and the Zn line at 213.856 nm.²⁶ At reduced source intensity, the magnitude of the diode array dark signal approaches the magnitude of the source signal. Also, at small source intensity, detector read-out noise may become significant. Finally, the transmittance of the air/acetylene flame

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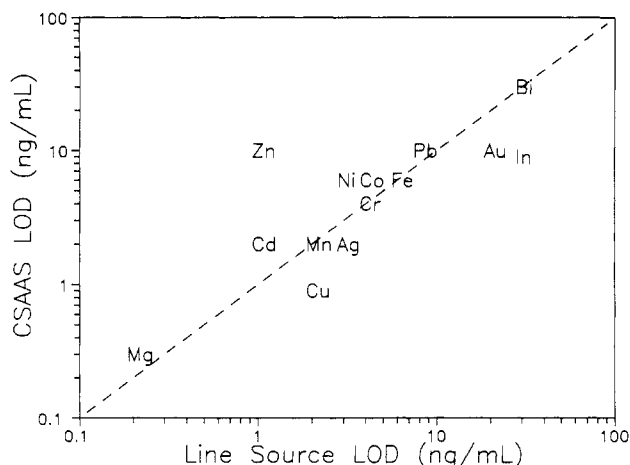


Figure 6. Comparison of limits of detection measured with the CSAAS system to those reported for conventional line source systems.³¹ For elements falling below the dashed line, the CSAAS detection limits are better than those reported for the line source.

also decreases at low wavelengths. The determination of Pb at 217.000 nm is also limited by these factors. The LOD observed for Pb with the current system at that wavelength is 40 ng/mL (a factor of 5 greater than the line source value). As a result, a lower LOD for Pb is observed at 283.305 nm with the present system. Nevertheless, for the 15 elements studied, six had a slightly worse LOD compared to the line source values, five had a slightly better LOD, and in four cases the LOD was the same for both techniques (Figure 6).

Simultaneous multielement analyses may be performed by employing compromise flame atomization parameters with a carefully selected wavelength window. The compromise flame conditions did not degrade the sensitivity of the technique significantly. The detection limits at the major absorption lines for the seven elements tested (Cd, Cu, Cr, Fe, In, Mn, Ni) were all within a factor of 2 of those observed in the single-element cases (Table II). Of greater concern is the selection of a wavelength region to be monitored. As many as six elements may be determined simultaneously at maximum sensitivity. For example, the strongest absorption lines for Bi, Sn, Te, Cd, Sb, and Ni (223.1, 224.6, 225.9, 228.8, 231.2, and 232.0 nm, respectively) fall within a single wavelength window. Similarly Mn, Pt, Pb, Mg, Sn, and Ga (279.5, 283.0, 283.3, 285.2, 286.3, and 287.4 nm) may be determined simultaneously at levels within a factor of 2 of their single-element detection limits. As demonstrated in Figures 2–4, many more elements may be determined simultaneously at reduced sensitivity. The determination of a greater number of elements at maximum sensitivity would require the use of several spectral windows. With the present system, the wavelength region can be changed in a matter of seconds, at least 10 different spectral windows can be monitored in a span of 5 minutes.

The linear dynamic range (LDR) is defined as the concentration range over which the analytical calibration curve is linear for a particular element. The lower limit of the LDR is taken as the LOD, and the upper limit is defined as the

concentration at which the measured absorbance falls 5% below the extrapolated linear portion of the calibration curve.³¹ Traditionally, CSAAS systems have been plagued with poor LDRs (less than 2 orders of magnitude) for measurements made at a single wavelength.^{2–7,13–15} Reasons for this limited range include the relatively high detection limits at the lower end and excessive amounts of stray light reaching the detector causing reduced sensitivity at the higher concentrations.¹⁵ For each element investigated with the present system, the linear dynamic range was approximately 3 orders of magnitude, roughly the same as typical line source values.³¹ The 1 order of magnitude extension of the LDR compared to previous CSAAS systems results directly from the improved LOD for each element.

Previous workers have obtained significant increases in the LDR (up to 5–6 orders of magnitude) by measuring the absorbance either at the wing of the absorption profile^{2–7,33} or at the center of the absorption profile of less sensitive atomic lines.¹⁵ The first method requires a large number of intensity measurements to be made over the absorption profile and may suffer from a time limitation.¹⁴ Moreover, the exact positions of sampling points along the absorption profile have to be predetermined and change during the analysis are not possible. The latter method has been performed with a CID detector. The LDR for iron in that case was at least 3 orders of magnitude. Similarly, the diode array system may offer extended LDRs by measuring the peak heights of several atomic lines for a single element. Iron, for example, has 15 absorption lines of different sensitivity in the region between 370 and 376 nm. By selection of four of these lines, the overall LDR of the technique spans 6 orders of magnitude (Table II). Actually, the same extended LDR is achieved by monitoring only two of those lines (371.994 and 374.336 nm). An LDR of 6 orders of magnitude was also obtained for cobalt, and other elements having more than one absorption line in a single 9-nm spectral window (Ni, Cu, Mn, etc.) should provide similar results.

In conclusion, the results reported here clearly demonstrate the advantages of the current CSAAS-PDA system over previously reported CSAAS designs: lower detection limits, LODs similar to line source LODs at wavelengths as low as 223 nm, larger linear dynamic ranges for a single calibration curve, simple extended LDR capabilities, and visual background correction methods. The present system offers all of the advantages of a line source AAS instrument with the added multielement capabilities of CSAAS.

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Registry No. Mg, 7439-95-4; Cu, 7440-50-8; Cd, 7440-43-9; Mn, 7439-96-5; Ag, 7440-22-4; Zn, 7440-66-6; Ni, 7440-02-0; Cr, 7440-47-3; Co, 7440-48-4; Fe, 7439-89-6; Pb, 7439-92-1; Au, 7440-57-5; In, 7440-74-6; Bi, 7440-69-9.

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