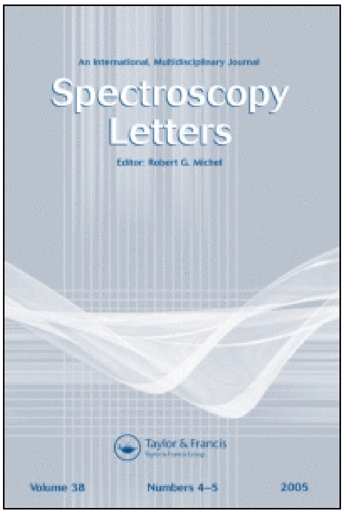

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CARBON FURNACE ATOMIC EMISSION SPECTROMETRY WITH A CONSTANT TEMPERATURE ATOMIZER

Key words: atomic emission, carbon furnace atomization, constant temperature atomization

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ABSTRACT

A constant temperature Woodriff type furnace is used as an excitation source in carbon furnace atomic emission spectrometry. Instrumental response is limited by blackbody background emission from the heater tube and can only be partially corrected for by the optical system employed. Sensitivity at various excitation temperatures represents a tradeoff between the temperature related population of the excited state and intensity of background emission. Absolute detection limits obtainable for selected transition metals are generally in the ng range and vary from 0.05 ng for Mn to 8.6 ng for Ni. Reproducibility at 50 times the detection limit is ± 5% RSD or better. No matrix interferences are noted for the peak area emission obtained at concentrations of 1% (v/v) chloride, nitrate, phosphate or sulfate.

INTRODUCTION

The emergence of the inert gas electrical plasma as an excitation source has renewed interest in elemental analysis by emission

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spectroscopy. The electrothermal atomizer (ETA) has received only minimal attention as an emission source, presumably due to its relatively low excitation energy and therefore minimal ability to excite species above the ground state. However, the ETA has real advantages over more conventional emission sources in that 1) excitation is accomplished without the complicating influence of the electrical conduction of highly ionized vapors, 2) the greater mean residence time of the atoms in the optical path,[1] and 3) relative freedom from ionization interferences.[2,3] In addition, the low excitation energy of the ETA produces a relatively uncomplicated emission spectrum; interelement spectral overlap problems which plague the higher energy excitation sources are sharply reduced with the furnace source. The utilization of commercial ramp type atomizers as an emission source has been documented by various researchers.[1,4-8] Detection limits obtainable with such systems are generally in the ng/ml range; after appropriate reduction of the background emission with effective optical design sensitivity is limited by residence time in the graphite tube. The Woodriff type constant temperature graphite rod atomizer possesses many characteristics that makes it conceptually a more efficient source than the ramp type. Of primary importance is the much longer mean residence time in the optical path [typically 10-40 sec[9] as compared to $\simeq$ 1 sec in ramp type atomizers][10] and the relative freedom of this source from matrix interferences.[11,12] The purpose of this manuscript is to quantitate the performance of a simple spectrometer and furnace interfaced as an emission system.

EXPERIMENTAL

The atomizer used was a Woodriff type, three phase constant temperature graphite rod furnace which is described in greater detail elsewhere.[13] The atom chamber was defined by the graphite heater rod which was 35 cm in length and had a bore of 8 mm. Samples were introduced into the atomizer in graphite cups that were pushed into the zone of active heating. Cups, atomizer tubes and other graphite components are made from Poco (Decatur, Texas) type AXF-5Q stock material. 100 μl samples were injected into the cups using a Centaur Model 78399-14 constant volume pipette and were dried under an infrared lamp for 30 min. All graphite cups used were cleaned by firing in the furnace at a temperature of 2350°C for 1 min prior to usage. Samples of standard solutions and the reagent blank were all prepared and analyzed in triplicate. The atomizer was equipped with quartz lenses at both ends of the optical path. Argon, introduced at the rate of 200 ml/min at a point located just above the sample introduction slot was used as the purge gas.

A medium dispersion Beckman DU spectrometer was used as the detector; to reduce background emission the entrance slit of the monochromator was shielded with a plate having an entrance port of 3 mm diameter. The distance between the quartz exit lens of the atomizer (focal length 10 cm) and the monochromator's entrance slit was adjusted to minimize background emission; for the system employed herein the optimum distance between these points was 15 cm. Emission response of the photomultiplier was converted to an integrated peak area with an electronic system designed by Dewalt and associates which was originally used for background correction in absorption analysis.[13] With this system, removal of the background emission component of the photomultiplier signal was accomplished either by altering the entrance slit width or the voltage offset in the voltage/frequency converter. Emission wavelength was set on the monochromator with the aid of appropriate single element hollow cathode lamps; the monochromator is then peaked on the line by using the atomic emission signal obtained during atomization of standard samples.

Tube wall temperature was measured at the midpoint of the heater tube length with an optical pyrometer. The pyrometer was focused on the inside of the tube through the exit lens. All standard solutions were prepared from reagent grade chemicals by dissolving the appropriate salt in either a nitric or sulfuric acid matrix. Working standards were prepared from the stock solution by dilution with doubly distilled water and were made 0.5% (v/v) in HNO_3. All acids used were Baker reagent grade.

RESULTS AND DISCUSSION

The magnitude of the analyte atomic emission signal depends on the atom concentration and the population of the excited state; given an effective means of eliminating background emission from the atomizer source the major limitation in emission intensity is the residence time and absolute size of the population of the excited state in the optical path. Sensitivity obtained by carbon furnace atomic emission spectroscopy using ramp type carbon atomizers is limited in some cases by the inability to populate sufficiently the higher energy levels of volatile elements before they leave the optical path;[1] for these species photomultiplier response is expected to fall off as furnace temperatures increase past a critical point. In the Woodriff design, this effect is dramatically diminished; one would therefore expect, assuming a Boltzman type distribution, an exponential relationship to exist between analyte emission intensity and temperature which is directly related to increased population of the excited state. Unfortunately, the inability of the present system to adequately correct for blackbody background emission from the atomizer tubes by optical means (which requires reduction of the width of the monochromator entrance slit to prevent integrator saturation) prevents the analyst from taking full advantage of the increased analyte emission. It is expected that photomultiplier response will increase up to a critical atomization temperature at which time the benefits of increased emission are offset by the decreasing amount of total light reaching the photomultiplier which is a direct result of having to decrease the entrance slit width to reduce the background signal. After this point, continued increase of atomization temperature produces rapidly decreasing system response. As illustrated in Figure 1, this type of behavior is observed for all analytes examined with maximum corrected emission occuring between 2000 and 2300°C. The close proximity of optimum excitation temperatures for the elements examined emphasizes the potential of the Woodriff design for simultaneous multielement analysis.

Optimized operating conditions for Co, Cu, Fe, Mg, Mn, Ni, Pb and Sn are summarized in Table 1. One readily notes the inverse relationship between wavelength at which analyte emission is measured and the bandwidth of the monochromator entrance slit which accurately reflects the wavelength dependence of the the system limiting background emission.[15] Detection limits, defined as two times the concentration equivalent to the standard deviation of replicate reagent blank analyses, are generally in the ng range. Sensitivities, defined in terms of the minimum reproducible integrated emission area (100 counts), is also in the ng range with greatest sensitivity being achieved for Mn (0.05 ng/100 counts) and the least for Ni (8.8 ng/100 counts). Reproducibility of the response at analyte concentrations 50 times the detection limit are generally 5% RSD or less. Linear dynamic range of the instrument for the species studies is four orders of magnitude or better; correlation coefficients calculated from linear

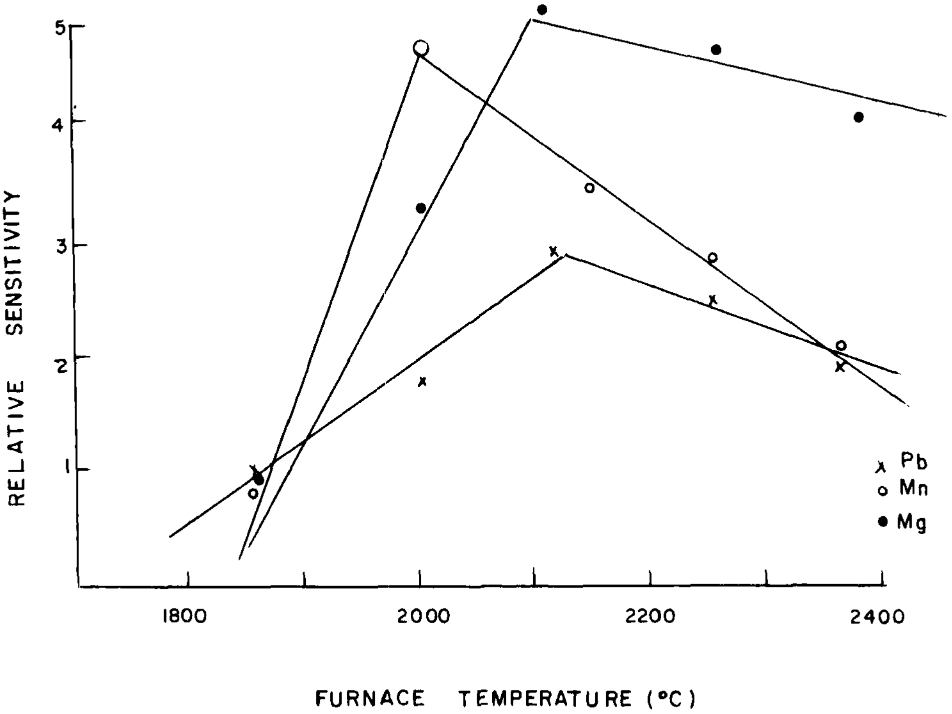

Figure 1. Relative instrumental sensitivity for Pb, Mn and Mg as a function of furnace temperature. Emission measured at 405.7, 403.1 and 285.2 nm, respectively, for Pb, Mn and Mg.

regression analysis of calibration data encompassing this large of a concentration range are, except for Mg, generally 0.999 or better as shown in Table 2. The somewhat poorer correlation of the Mg data is related to what appears as a break in slope in the calibration plots at intermediate (1 ppm) concentration. At low concentration, instrument response and analyte concentration exhibit a 1/1 relationship (that is, a tenfold increase in analyte concentration causes a tenfold increase in response) while above 1 ppm the response factor degrades to approximately 0.25. This behavior reflects the onset of self reversal at the 1 ppm concentration level.

TABLE 1

Temperature Optimized Characteristics of the Furnace Emission Source

Element	Wave-length (nm)	$T_{optimum}$ (°C)	Bandwidth (nm)	Sensi-tivity (ng/100 cnts)	Detection Limit (ng)	Reprodu-cibility[1] (% RSD)
Co	345.3	2300	0.066	2.51	9.5	4.4
Cr	425.1	2300	0.030	0.70	0.53	3.6
Fe	371.9	2000	0.078	1.57	5.6	5.7
Mg	285.2	2100	0.290	2.24	4.0	2.5
Mn	403.1	2000	0.046	0.05	0.13	4.5
Ni	341.4	2350	0.060	8.59	12.6	4.6
Pb	405.7	2100	0.632	7.45	8.0	3.7
Sn	286.3	2300	0.165	4.13	4.7	4.0

[1] at analyte concentration 50 times the detection limit

TABLE 2

Calibration Data

Element	Concentration range (ppm)	Correlation Coefficient
Co	0.1 - 100	.99988
Cr	0.01 - 10	.99966
Fe	0.1 - 100	.99998
Mg	0.01 - 5	.95187
Mn	0.01 - 100	.99993
Ni	1. - 1000	.99981
Pb	0.1 - 50	.99989
Sn	0.1 - 100	.99981

Matrix interferences, although reportedly decreased in magnitude in the constant temperature furnace,[11,12] are important problems encountered in sample analysis by carbon furnace atomic absorption techniques. In order to determine what effects common anions (Cl^-, NO_3^-, SO_4^{-2}, PO_4^{-3}) have on the emission characteristics of Co, Fe, Mg, Mn and Pb, samples containing 100 ng or 1 μg analyte in a matrix of either 1% (v/v) acid or deionized water are analyzed in replicate under optimized conditions. As illustrated in Table 3, the integrated, reagent blank corrected emission signal for all analyte species vary, for all matrices tested, by no more than the relative uncertainty of the individual determinations. It is noted, however, that at the 100 ng analyte level, the presence of chloride in the sample matrix does decrease both Pb and Fe emission somewhat (roughly 5%) while at a tenfold increase in analyte concentration the signal reduction is not observed. We suggest that matrix effects would appear to be minimal under the conditions used for the analytes documented herein.

Given the critical nature of the relationship between the level of backbody background radiation from the atomizer tube and the ability to detect the emission from analyte species, it is important to limit the magnitude of this effect. Using much smaller atomizer tubes for commercial ramp type atomizers, Littlejohn and Ottaway were able to limit the wall emission access to the monochromator by placing a telephoto lens between the atomizer and monochromator thereby reducing tube wall emission to a sharply focused ring inside of which the entrance slit of the monochromator was mounted.[15] To produce this effect a lens was sharply focused ring inside of which the entrance slit of the monochromator was mounted.[15] To produce this effect a lens was required with a focal length four times longer than the carbon excitation tube; given the length of the average Woodriff atomizer tube the

TABLE 3

Effect of Sample Matrix on Integrated Emission Signal

Species	Integrated Emission Signal (counts)[1]				
Matrix	H_2O	HNO_3	HCl	H_2SO_4	H_3PO_4
a) 100 ng analyte					
Co	4527(147)	4399(110)	4459(50)	4589(94)	4535(63)
Fe	5750(29)	4730(44)	5660(31)	5483(47)	5304(74)
Mg	9220(87)	9172(74)	8964(94)	9165(91)	9273(34)
Mn	196872(297)	195989(626)	196537(401)	197055(79)	197045(159)
Pb	1471(11)	1480(15)	1372(20)	1466(18)	1420(39)
b) 1 µg analyte					
Co	38098(1285)	38393(501)	38555(565)	38310(1100)	38471(515)
Fe	63508(238)	63258(510)	62738(569)	64179(472)	63698(338)
Mg	44883(144)	45050(114)	44407(533)	44512(1330)	43898(816)
Mn	1074572(1458)	1075779(4381)	1070876(801)	1074731(2006)	1072220(1930)
Pb	11095(68)	11035(128)	11203(451)	11134(62)	11000(23)

[1] mean (STD)

adoption of this type of approach was difficult. Instead of focusing furnace tube emission into a distinct ring, the present apparatus disperses this emission around the center tube image producing a large disk image on the monochromator. The focal length of the lens used was considerably smaller than the length of the atomizer tube; therefore, complete dispersion of the tube emission could not be achieved. Background emission levels were thus somewhat higher than one might have hoped. In addition, background emission from the tube can enter the monochromator indirectly as both reflections off the entrance lens of the furnace or as the result of Rayleigh scatterring of furnace wall radiation by atoms or molecules in the vapor phase of the furnace. The latter problem is, however, enhanced by the long length of the Woodriff atomizer tube. It is felt that through modification of the system's optical components as well as the utilizaiton of a more suitable monochromator (higher dispersion) a substantial decrease in background emission level and therefore greater instrumental sensitivity can be achieved.

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REFERENCES

1. D. Littlejohn and J. M. Ottaway, Anal. Chim. Acta, 109, 139 (1979).
2. J. M. Ottaway, F. Shaw, Analyst, 104, 208 (1979).
3. R. C. Hutton, Ph.D. Thesis, University of Strathclyde, Glasgow, England, 1977.
4. D. Littlejohn and J. M. Ottaway, Anal. Chim. Acta, 98, 279 (1978).
5. J. M. Ottaway and F. Shaw, Appl. Spectrosc., 31, 12 (1977).
6. D. Littlejohn and J. M. Ottaway, Analyst, 103, 662 (1977).
7. M. S. Epstein, J. R. Moody, T. J. Brady, T. C. Rains and I. L. Barnes, Anal. Chem., 50, 874 (1978).
8. D. Littlejohn and J. M. Ottaway, Analyst, 104, 1138 (1979).
9. R. Woodriff, M. Marinkovic, R. A. Howald and I. Eliezer, Anal. Chem., 49, 2008 (1977).
10. R. E. Sturgeon, D. L. Chakrabarti and P. C. Bertels, Anal. Chem., 47, 1250 (1975).
11. L. R. Hageman, J. A. Nichols, P. Viswanadham and R. Woodriff, Anal. Chem., 51, 1406 (1979).
12. L. R. Hageman, A. Mubarak and R. Woodriff, Appl. Spectrosc., 33, 226 (1979).

13. F. G. Dewalt, J. R. Amend and R. Woodriff, Appl. Spectrosc., 35, 176 (1981).

14. F. G. Dewalt, J. R. Amend and R. Woodriff, Appl. Spectrosc., 35, 176 (1981).

15. D. Littlejohn and J. M. Ottaway, Analyst, 102, 553 (1977).

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