Table IV. Effect of High Concentrations of Trace Elements on Co Recovery

μg of Element in digest				
Fe	Cu	Zn	Mn	Recovery, %
1526	102	405	1215	115.7
836	52	205	615	113.0
146	2	205	615	111.9
73	1	202	608	117.2
73	1	2	608	119.6
376	17	65	195	111.1
146	7	25	75	94.6
836	52	5	15	100.5
73	1	202	8	105.8

cal flask for 15–20 min. Duplicate recoveries of 102.2 and 105.7% were obtained when this was done in the presence of the highest levels of trace elements listed in Table IV. A disadvantage of this modification was that the slow liberation of O_2 which occurred after about 1½ hr, if a precipitate was present, might be a safety hazard. Replacement of H_2O_2 with ascorbic acid (*16*) might be a satisfactory way of avoiding this hazard.

None of the macro elements interfered seriously with the proposed procedure. Recoveries ranging from 101.3 to 106.7% were obtained when Ca (0–25000 μg) and Mg (0–4000 μg) were added together in various proportions to 0.5 g of wheat. The recovery was 100.2% when 50000 μg of K and 10000 μg of P were added to 1 g of wheat straw.

CONCLUSION

The greater sensitivity of the furnace has allowed the development of a faster, simpler procedure for measuring Co in plant material than either flame atomic absorption or colorimetry because it needs only 0.5-g samples. At the same time, there has been no loss in accuracy or precision when compared with these other methods. While the heated graphite atomizer has been used for the development of this method, the new procedure, or a modification of it, should be applicable to other alternative furnaces.

In a study of cobalt distribution in plants, Wilson and Hallsworth (*17*) were unable to measure the Co in various plant parts because their analytical technique did not have sufficient sensitivity. The proposed procedure should allow such experiments to be carried out since only a small amount of plant material is needed for analysis.

ACKNOWLEDGMENT

The author thanks A. D. Robson for helpful, constructive discussion in both the development of the method and the preparation of the manuscript.

LITERATURE CITED

(1) E. J. Underwood, "Trace Elements in Human and Animal Nutrition", 3rd ed., Academic Press, New York, N.Y., 1971, p 150.
(2) H. R. Marston and D. W. Dewey, *Aust. J. Exp. Biol. Med. Sci.*, **18**, 343 (1940).
(3) D. W. Dewey and H. R. Marston, *Anal. Chim. Acta.*, **57**, 45 (1971).
(4) W. J. Simmons, *Anal. Chem.*, **45**, 1947 (1973).
(5) J. Jago, P. E. Wilson, and B. M. Lee, *Analyst*, **96**, 349 (1971).
(6) A. L. Gelman, *J. Sci. Food Agric.*, **23**, 299 (1972).
(7) J. S. Gladstones and J. F. Loneragan, *Aust. J. Agric. Res.*, **18**, 427 (1967).
(8) H. Massman, *Spectrochim. Acta., Part B*, **23**, 215 (1968).
(9) D. A. Segar, *Int. J. Environ. Anal. Chem.*, **3**, 107 (1973).
(10) C. M. Johnson and A. Ulrich, "Analytical Methods for Use in Plant Analysis", *Bull. Calif. Agr. Exp. Stn.*, **766**, 32 (1959).
(11) J. E. Allen, "The Preparation of Agricultural Samples for Analysis by Atomic Absorption Spectroscopy", Varian Aerograph/Varian Techtron Publication, 1969, pp 7 and 13.
(12) K. Everett and F. A. Graf, Jr., "Handbook of Laboratory Safety", 2nd ed., The Chemical Rubber Co., Cleveland, Ohio, 1971, pp 265–276.
(13) E. Boyland, *Analyst*, **71**, 230 (1946).
(14) E. B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, N.Y., 1959, p 420.
(15) W. J. Youden, "Statistical Methods for Chemists", 1st ed., Wiley, New York, N.Y., 1957, p 40.
(16) T. C. Z. Jayman and S. Sivabramaniam, *Analyst*, **99**, 296 (1974).
(17) S. B. Wilson and E. G. Hallsworth, *Plant Soil*, **23**, 60 (1965).

RECEIVED for review May 5, 1975. Accepted June 30, 1975. Work supported by the Western Australian State Wheat Industry Research Committee.

Simultaneous Multielement Determination of Trace Metals by Microwave Induced Plasma Coupled to Vidicon Detector: Carbon Cup Sample Introduction

Fred L. Fricke

Cincinnati District Food and Drug Administration, 1141 Central Parkway, Cincinnati, Ohio 45202

Oliver Rose, Jr., and Joseph A. Caruso[1]

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

In numerous laboratories, there is a need for simultaneous multielement analysis, because the time and cost of single element analyses are prohibitive. It has been shown that inductively coupled plasma–optical emission spectographic systems are useful for simultaneous multielement analysis (*1, 2*). The use of low power microwave induced argon plasma for spectral excitation of the elements also has been well documented (*3–17*). When coupled to a multichannel spectrometer, the microwave induced plasma has potential for multielement trace analysis.

[1] Author to whom correspondence should be addressed.

Morrison and coworkers (*18*) developed a multielement flame emission system using a vidicon tube detector and an optical multichannel analyzer (OMA). They provide an excellent description of this particular instrument. Nixon et al. (*19*) have developed a tantalum strip sampling introduction device for use with an inductively coupled plasma.

This paper describes the combination of a microwave induced plasma with a carbon cup sampling device. A comparison is made between this apparatus and a tantalum strip sampling device coupled to a microwave induced plasma. In addition, a preliminary study of the potential appli-

cability of the microwave induced plasma coupled to a vidicon detector for simultaneous multielement trace metal analysis is presented.

EXPERIMENTAL

Apparatus. The instrumentation utilized is listed in Table I. The tantalum strip vaporization device is similar in design to the device described by Nixon et al. (*19*). The carbon cup vaporization device also is similar except the tantalum strip assembly was replaced with a carbon cup assembly consisting of a carbon cup, support electrodes (Varian Techtron), and two fixed support blocks. The fixed support blocks, similar to those furnished with a Varian Techtron carbon rod atomizer (*20*), were constructed with the following modifications: electrical connecting shafts, 25 mm long, were placed on the bottom of each block; the knurled knobs were replaced with Phillips head screws; and a water circulating system was installed to pass cooling water through the entire block. The top half of the carbon cup was removed to allow more rapid heating.

Reagents. Stock solutions were prepared from Fisher atomic absorption standards or, alternatively, by dissolving pure metals or reagent grade salts in acid diluted with deionized water.

Procedure. After the argon flow rate was set at 900 ml/min, the plasma was initiated with a Tesla coil and the microwave power was set at 45 watts. Five microliters of a solution containing elements of interest were pipetted (Autopette 5-μl pipet) into the carbon cup or onto the tantalum strip, and a low current was passed through the cup/strip for three minutes to resistively heat (drying temperature ~70 °C) and vaporize the water without extinguishing the plasma. Then, the cup/strip was rapidly heated using a large current vaporizing the elements into the argon plasma.

For the single element analysis, the vaporization temperature was optimized for each element. Radiation from an appropriate hollow cathode lamp was reflected into the monochromator using a removable mirror to optimize the analytical line. The emission was detected and the amplified signal was recorded on a strip chart recorder. The peak heights were measured to determine detection limits.

For the simultaneous multielement determination, the carbon cup was the sample introduction device with a compromise element vaporization temperature of approximately 2000 °C. The vidicon/OMA unit was used to measure the emission signals in a 700-Å window as provided by the polychromator. The resulting emission signals of the elements as they passed through the plasma were accumulated for 4.1 seconds (125 machine cycles with no delay cycles) and stored in memory A of the OMA. The background signal (signal for a blank firing of the carbon cup) was accumulated for 4.1 seconds and stored in memory B. The memory B was then subtracted from memory A and the 700-Å emission spectrum was displayed on the monitor and recorded. Finally, the peak height of each analytical line vs. concentration was plotted to give the analytical curve.

RESULTS AND DISCUSSION

A comparison of detection limits (signal-to-noise ratio of two) for several elements using the carbon cup and tantalum strip vaporization systems coupled to the microwave plasma in the single wavelength mode is shown in Table II. These values were determined by measuring the signal-to-noise ratio with a sample size of approximately ten times the detection limit and calculating the sample size which would have generated a signal-to-noise ratio of two. The lower detection limits for the carbon cup system are due in part to the analyte being restricted to the small area of the carbon cup (i.d.—3 mm) compared to the larger area caused by the solution spreading across the tantalum strip (length—33 mm). This restriction to the smaller area apparently provides a greater analytical throughput per unit time of analyte to the plasma and subsequently a greater emission signal. Other advantages of the carbon cup over the tantalum strip include: the carbon cup has a higher temperature capability allowing determination of less volatile elements; the carbon does not oxidize as readily as the tantalum does; elements such as cobalt and nickel which react with the tantalum surface (*22*) can be determined; and spectral interference from tantalum emission is eliminated. A disadvantage of the carbon cup may be the formation of relatively non-volatile carbides at high temperatures.

Table I. Experimental Instrumentation

Excitation system	
2450-MHz microwave generator	Opthos Instrument Co.
Microwave coupling cavity No. 5	NBS Report (*21*), Opthos Instrument Co.
Quartz tube	1.3-mm i.d.
Vaporization system	
Tantalum strip assembly	Barnes Engineering Co.
Carbon cup assembly	Described in text
Power supply	Laboratory constructed
Dispersive optics and detection for single wavelength determination	
Monochromator	Jarrell-Ash, 0.5-m Ebert with 1180 g/mm grating blazed for 3000 Å. Reciprocal linear dispersion 16 Å/mm in the first order
Entrance slit	Fixed slit, 100-μ wide, straight edge
Detector	IP28 photomultiplier tube mounted at the 150-μ exit slit
Electronics	Jarrell-Ash MVAA 82500 Atomic Absorption Spectrometer used in the emission mode
Readout	Hewlett-Packard Model 7101B Recorder
Dispersive optics and detection for multielement determination	
Polychromator	Princeton Applied Research Model 1208, 0.3-m Ebert with 590 g/mm grating blazed at 3000 Å. Reciprocal linear dispersion 55 Å/mm in the first order
Entrance slit	Fixed slit, 25-μ wide, straight edge
Detector	Princeton Applied Research Model 1205D Intensified vidicon detector head. Type B plastic UV-scintillator, 0.1-mm thick
Optical Multichannel Analyzer	Princeton Applied Research Model 1205A
Oscilloscope Monitor	Tektronix Model 604
Recorder	Hewlett-Packard Model 7101B

An illustration of the precision obtained with the carbon cup in the single wavelength mode is shown in Figure 1. This figure represents the recorder tracings for 10 replicate determinations of Bi at 10 times the detection limit. The relative standard deviation is 4.0%.

A microwave induced plasma coupled to a vidicon detector with carbon cup sample introduction has potential for simultaneous multielement trace analysis. Typical analytical curves obtained using this system are shown in Figure 2. Each point on the curve is an average of five determinations. The elements, Se, As, Zn, Sb, Bi, Sn, and Cd were determined in the 1900- to 2600-Å window and Mn, Cu, and Sn in the 2750- to 3450-Å window. A typical spectrum for

Table II. Absolute Detection Limits

Element	Wavelength, Å	Carbon cup, ng[a]	Tantalum strip, ng[a]
As	1936.96	0.2	0.6
Se	1960.26	0.1	0.6
Cd	2288.02	0.004	0.02
Zn	2138.56	0.005	0.02
Pb	4057.83	0.08	0.3
Sb	2311.47	0.2	0.5
Sn	2863.33	0.3	1.1
Bi	2230.61	0.1	0.2
Be	2348.61	0.1	...
Co	2407.25	0.07	...
Ni	2320.03	0.1	...

[a] 5-μl sample volume.

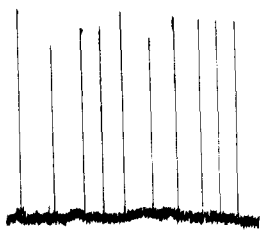

Figure 1. Recorder tracing of the emission signals for 1 ng Bi illustrating reproducibility of the carbon cup/microwave induced plasma system

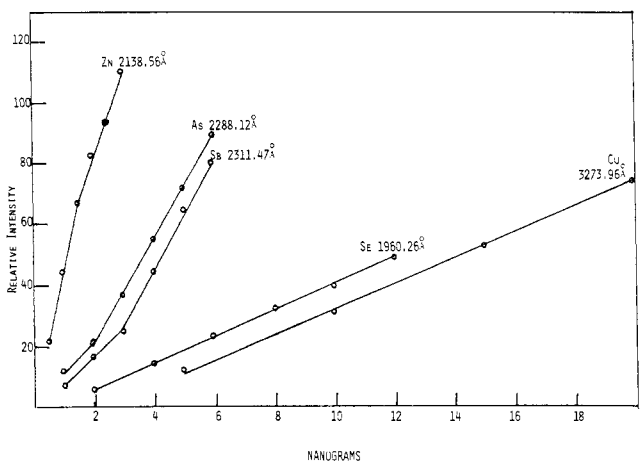

Figure 2. Typical analytical curves for the carbon cup/microwave induced plasma/vidicon system

the 1900- to 2600-Å window is shown in Figure 3. Arsenic and cadmium could not be determined simultaneously in this window because of the spectral overlap at the 2288.0-Å line. The background signal interfered with the 1937.0-Å As line. The 3093.4-Å Ar line saturated the vidicon prohibiting the determination of Mo at the 3132.6-Å line. Total correction for the background signal could not be accomplished because the start of the signal accumulation by the OMA was not synchronized with the firing of the carbon cup and because there was a random noise component present in the signals. The former problem could be readily alleviated, thereby improving precision, by using appropriate logic circuitry to permit the OMA to control the carbon cup firing mechanism.

This preliminary study indicates that a microwave induced plasma coupled to a vidicon detector has potential

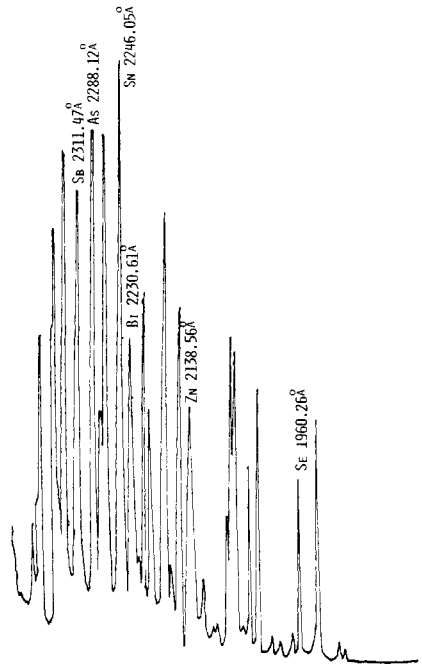

Figure 3. Multielement emission spectrum from 1900 to 2600 Å

for simultaneous multielement analysis. Future work will focus on optimization and application to samples with complex matrices.

ACKNOWLEDGMENT

We are grateful to Princeton Applied Research Corporation for loan of the vidicon instrumentation for a one-week period.

LITERATURE CITED

(1) V. A. Fassel and R. N. Kniseley, *Anal. Chem.*, **46,** 1110 A (1974).
(2) *Ibid.*, p 1155 A and references therein.
(3) A. J. McCormack, S. C. Tong, and W. D. Cooke, *Anal. Chem.*, **37,** 1470 (1965).
(4) J. H. Runnels and J. H. Gibson, *Anal. Chem.*, **39,** 1398 (1967).
(5) D. N. Hingle, G. F. Kirkbright, and R. M. Bailey, *Talanta*, **16,** 1223 (1969).
(6) H. E. Taylor, J. H. Gibson, and R. K. Skogerboe, *Anal. Chem.*, **42,** 876 (1970).
(7) *Ibid.*, p 1569.
(8) K. F. Fallgatter, V. Svoboda, and J. D. Winefordner, *Appl. Spectrosc.*, **25,** 347 (1971).
(9) S. Murayama, H. Matsuno, and M. Yamamoto, *Spectrochim. Acta*, **23B,** 513 (1968).
(10) M. Yamamoto and S. Murayama, *Spectrochim. Acta*, **23A,** 773 (1967).
(11) H. Kawaguchi, M. Hasegawa, and A. Mizuikie, *Spectrochim. Acta*, **27B,** 205 (1972).
(12) K. W. Busch and T. J. Vickers, *Spectrochim. Acta*, **28B,** 85 (1973).
(13) K. M. Aldous, R. M. Dagnall, B. L. Sharp, and T. S. West, *Anal. Chim. Acta*, **54,** 233 (1971).
(14) F. E. Lichte and R. K. Skogerboe, *Anal. Chem.*, **45,** 399 (1973).
(15) L. R. Layman and G. M. Hieftje, *Anal. Chem.*, **47,** 194 (1975).
(16) H. Kawaguchi and D. Auld, *Clin. Chem.*, **21,** 591 (1975).
(17) R. J. Watling, *Anal. Chim. Acta*, **75,** 281 (1975).
(18) K. W. Busch, N. G. Howell, and G. H. Morrison, *Anal. Chem.*, **46,** 575 (1974).
(19) D. E. Nixon, V. A. Fassel, and R. N. Kniseley, *ibid.*, p 210.
(20) J. P. Matousek, *Amer. Lab.*, p 45 (June 1971).
(21) F. C. Fehsenfeld, K. M. Evenson, and H. P. Brodia, *NBS Rept.*, 8705 (1964).
(22) N. S. McIntyre, M. G. Cook, and D. G. Boase, *Anal. Chem.*, **46,** 1983 (1974).

RECEIVED for review April 7, 195. Accepted June 2, 1975. O.R. and J.A.C. acknowledge the National Science Foundation and the National Institute of Occupational Safety and Health for partial support of this work with research grants GP 36478 and OH 00415.