



Detection of Aqueous Metals Using a Microglow Discharge Atomic Emission Sensor

Michael E. Zorn,^{1,*} Chester G. Wilson,² Yogesh B. Gianchandani,³ and Marc A. Anderson⁴

¹Department of Natural and Applied Sciences (Chemistry), University of Wisconsin – Green Bay, 2420 Nicolet Drive, Green Bay, WI 54311

²Department of Electrical Engineering, Louisiana Tech University, PO Box 10137, Ruston, LA 71272

³Department of Electrical Engineering and Computer Science, University of Michigan – Ann Arbor, 1301 Beal Avenue, Ann Arbor, MI 48109

⁴Environmental Chemistry and Technology Program, University of Wisconsin – Madison, 660 North Park Street, Madison, WI 53706

(Received: July 16, 2004. Accepted: July 27, 2004)

In this study, an atmospheric pressure open-air microglow discharge atomic emission sensor has been used to qualitatively and quantitatively determine selected aqueous metal analytes. The microglow source utilizes a high purity graphite anode, while the non-flowing electrolyte solution itself acts as the cathode. Emission is monitored using a commercial fiber optic-based spectrometer. The microglow sensor has been used to qualitatively determine 20 environmentally relevant metal analytes (Li, Be, B, Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Ba, Tl and Pb). The technique shows relatively low background emission, except in the wavelength range of 280–390 nm. Quantitative determination of sodium was also conducted with and without the use of an internal standard. The potassium internal standard improved the precision of the technique and resulted in detection limits that were approximately a factor of two lower than without the correction.

Keywords: Microglow Discharge Sensor, Atomic Emission Spectroscopy, Metals, Water Analysis.

1. INTRODUCTION

Atomic emission spectroscopy (AES) is a versatile method for determining the presence and concentration of metals in aqueous samples. Analytes introduced into an excitation source absorb energy and subsequently release that energy in the form of electromagnetic radiation. The spectrum of a gaseous atomic species is specific to that individual element and consists of well-defined narrow emission lines. Excitation sources include flames, plasmas (both inductively coupled and direct current), electric arc, and electric spark. Atomic emission spectroscopy has an advantage over atomic absorption spectroscopy (AAS) because AES is capable of simultaneous multi-element analyses,

whereas AAS requires utilization of an independent radiation source that is specific for each individual element of interest. Atomic emission techniques are routinely used to analyze for numerous trace elements of environmental significance.¹

Development of small-scale versions of atomic and molecular emission-based analytical devices has been the focus of increasing research in recent years.^{2–26} The excitation sources associated with these devices are often described as “glow discharges” or, if operated at atmospheric pressure, they can be described as “atmospheric pressure glow discharges.” Glow discharges have the ability to operate at low power, ranging from tens of W down to as low as 9 mW.²⁰ A number of researchers have reported using miniaturized molecular emission sources as gas chromatographic detectors,^{19–23} while other previous studies

*Corresponding author; E-mail: zornm@uwgb.edu

have utilized these devices for atomic emission to determine heavy metals in aqueous solutions.^{2-5,7-18,24,26}

Recently, several of the authors have described efforts toward the development of a micromachined liquid electrode spectral emission chip (LEd-SpEC) for the purpose of determining aqueous metals.^{14,17} The LEd-SpEC devices have been used to determine Na, Al, Cr, and Pb. Initial designs were fabricated using a four mask process and employed the use of dual liquid electrodes, water sample reservoirs, microchannels for sample delivery, and a commercially available fiber optic-based spectrophotometer.¹⁴ Subsequent devices have been fabricated that incorporate a blazed grating and CCD (charge coupled device) detector in the overall assembly.¹⁷ Two separate versions have been developed; the planar version is constructed from multiple layers of glass to allow for ease of microfabrication, while the low-cost capillary tube version is intended for non-lithographic manufacturing. It has been shown that the dominant delivery mechanism with the LEd-SpEC devices is sputtering from the cathode rather than thermal volatilization.¹⁴ Additional specific physical characteristics (e.g. breakdown voltage as a function of electrode spacing, etc.) of the LEd-SpEC devices have also been previously reported.^{14,25} An example of a LEd-SpEC device is shown in Figure 1.

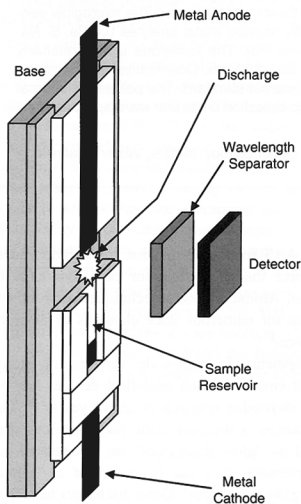


Figure 1. Schematic of a planar microglow discharge device that is constructed to allow for subsequent manufacture using microfabrication techniques. An additional planar component required to contain the water sample in the sample reservoir is not shown for purposes of clarity.

The purpose of this paper is to evaluate the qualitative and quantitative performance of a non-lithographic atmospheric pressure open-air microglow discharge atomic emission sensor comprised of a glass capillary sample cell connected to a stainless steel cathode; a high purity graphite rod positioned above the glass capillary tube acts as the anode. Qualitative performance is demonstrated by observing emission lines from 20 different environmentally relevant metal analytes. Quantitative performance is demonstrated by determining sodium with and without the use of an internal standard. The ultimate goal of this research is to develop a microglow discharge atomic emission sensor that could be used to measure the real-time concentration of aqueous metals. The sensor should be field portable (or even operated *in situ*), reliable, inexpensive, and simple to maintain and operate.

2. EXPERIMENTAL SECTION

Metal Standards. The qualitative portion of this study utilized commercially obtained metal standards at a concentration of 1000 mg/L (SPEX Industries, Inc., Edison, NJ), in a 2% nitric acid matrix unless otherwise noted. Specifically, standards of Be, B (pure water matrix), Na, Mg, Al, K, Ca, Cr, Mn, Co, Ni, Cu, Zn, Ag, Ba, and Tl were commercially obtained. Additional metal standards for the qualitative experiments (at concentrations of 1000 mg/L) were prepared by dissolving reagent grade solids in 6 mL of 1:1 nanopure water to concentrated nitric acid (Certified ACS PLUS Grade, Fisher Scientific, Pittsburgh, PA). After dissolution of the solids, the solutions were diluted to a final volume of 100 mL with nanopure water, resulting in a 2% nitric acid matrix. Specific solids used to prepare these standards were Li_2CO_3 (Mallinckrodt, Inc., St. Louis, MO), Fe metal wire (Allied Chemical Corp., Morristown, NJ), Cd metal (Alpkem Corp., Clackamas, OR), and $\text{Pb}(\text{NO}_3)_2$ (Fisher Scientific, Pittsburgh, PA).

Sodium and potassium standards were prepared fresh for the quantitative portion of this study. Reagent grade NaCl (ACS Grade, Fisher Scientific, Pittsburgh, PA) and KCl (ACS Grade, Fisher Scientific, Pittsburgh, PA) were dried at 125°C and stored in a desiccator prior to weighing. Stock solutions containing 1000 mg/L in 2% nitric acid were prepared from the pure solids. These stock solutions were then used to prepare individual standards at concentrations of 0.1, 0.5, 1, 5, 10, 50 and 100 mg/L Na. The overall ionic character of the individual standards was dominated by the 2% nitric acid matrix; the ionic strengths ranged from 0.475 M for the lowest sodium standard to 0.476 M for the highest standard.

Microglow Apparatus. A manual loading microglow discharge apparatus was fabricated and tested in this study. A schematic of the overall apparatus is shown in Figure 2. This design utilized a capillary-tube sample reservoir with an attached cathode as shown in Figure 3. This liquid electrode component was fabricated from a short section of

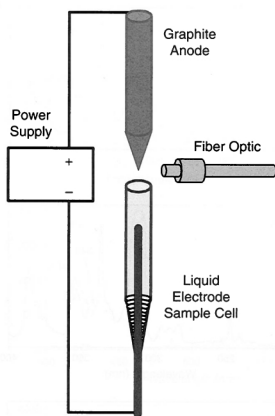


Figure 2. Schematic of the overall microglow discharge experimental setup.

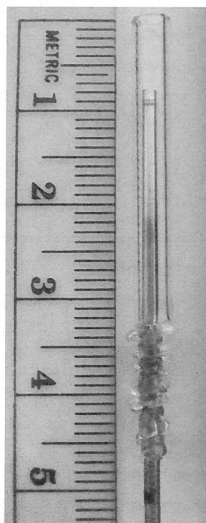


Figure 3. Cathode portion of the liquid electrode capillary-tube microglow discharge device used in this study. This component was fabricated from a short section of borosilicate glass capillary tubing that was thermally bonded at one end to a solid stainless steel shaft. The major scale of the ruler is centimeters.

borosilicate glass capillary tubing (4 mm O.D. \times 2.4 mm I.D.) that was thermally bonded at one end to a solid stainless steel shaft (316 type, 1/16" O.D., McMaster-Carr, Elmhurst, IL). The capillary tube was completely filled with sample (by manually pipetting into the open end) prior to insertion into the overall apparatus. A graphite anode (Alfa AESAR, SPK grade, Ultra "F" 99.9995% purity, 6.15 mm diameter \times 152 mm long) was sharpened to a point and positioned 0.8 mm above the filled capillary tube. A ballast resistor regulated high voltage DC power supply (Model P05HP12, Acopian, Easton, PA) provided 2.5 mA of current during formation of the microglow discharge.

Each sample was analyzed by manually filling the tubular sample reservoir, repositioning the graphite anode and fiber optic near the top of the sample reservoir, setting the current, and increasing the voltage until the microglow discharge was initiated. The voltage required to initiate the discharge, or the "breakdown voltage," varied between \sim 2.0–2.5 kV depending on the sample composition and the spacing between the anode and the top of the water sample. This resulted in a power consumption of 5.0–6.3 W. A given discharge event sequence lasted \sim 15 sec. At this time, the liquid in the capillary tube was reduced to a level that was at or below the level of the stainless steel shaft (\sim 0.3 mL of sample was consumed during the analyses).

Spectrometer. Emission from the microglow discharge was monitored using a commercially available fiber optic spectrometer (Model USB2000, Ocean Optics Inc., Dunedin, FL). The end of the fiber optic was positioned \sim 1 mm from the microglow discharge as shown in Figure 2. The spectrometer utilized a Sony ILX511 shallow-well linear CCD-array detector with 2084 pixels and an optical range of 200–850 nm. The spectrometer was plugged into the USB port of a computer that was subsequently used to analyze the spectra. Each saved spectrum was obtained by averaging 10 individual spectra, each having an integration time of 100 msec, unless otherwise noted. The spectrometer was calibrated with respect to wavelength prior to conducting the microglow emission experiments. Sodium was quantified using the emission intensity at 589.4 nm, and potassium was quantified using the emission intensity at 766.1 nm.

3. RESULTS AND DISCUSSION

Qualitative Analysis. Qualitative evaluation of the atmospheric pressure open-air microglow discharge atomic emission source was accomplished by analyzing 20 different environmentally relevant¹ metal standards in a 2% nitric acid matrix (unless otherwise noted in the Experimental Section) using the manual loading design. All samples contained the metal analyte at a concentration of 1000 mg/L and were collected using a signal integration time of 100 msec with the exception of Na (10 msec) and Tl (25 msec). Emission spectra for these elements using the microglow discharge sensor are shown in Figures 4–6.

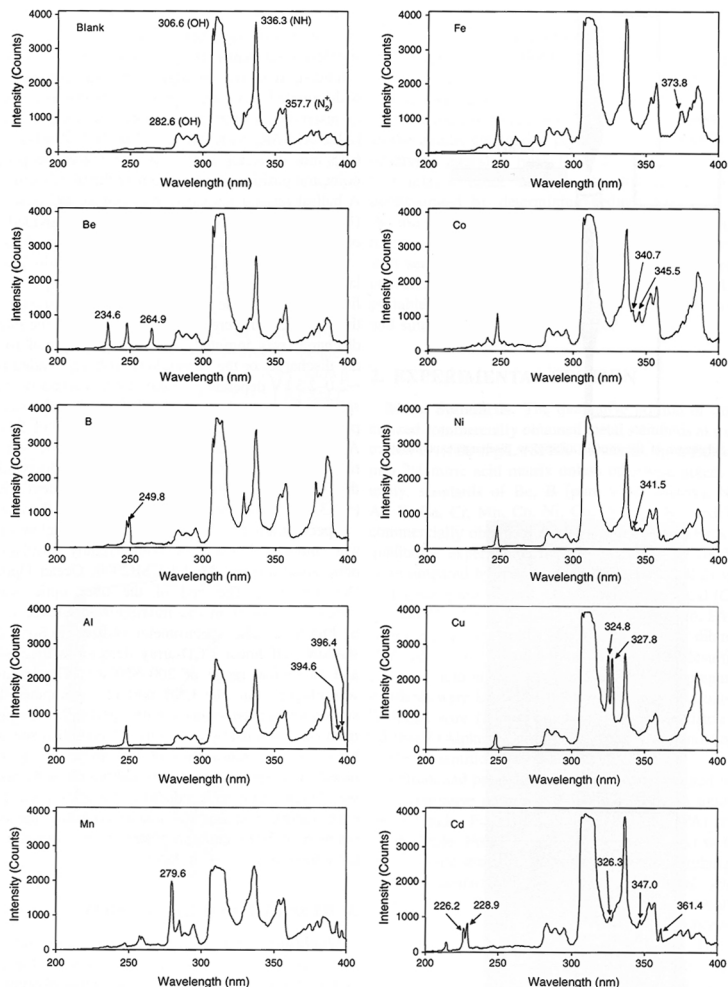


Figure 4. Emission spectra (200–400 nm) of selected environmentally relevant elements collected using the microglow discharge device described in this study. Selected emission lines are labeled.²⁷ A 2% nitric acid blank is included for reference.

The spectra are grouped according to the region where major emission lines were observed; 200–400 nm in Figure 4, 400–600 nm in Figure 5, and 600–800 nm in Figure 6. Emission lines for the individual metals are given

in the figures; theoretical wavelengths can be found in the CRC Practical Handbook of Spectroscopy.²⁷

An emission spectrum from a blank sample containing only 2% nitric acid is also shown in Figures 4–6

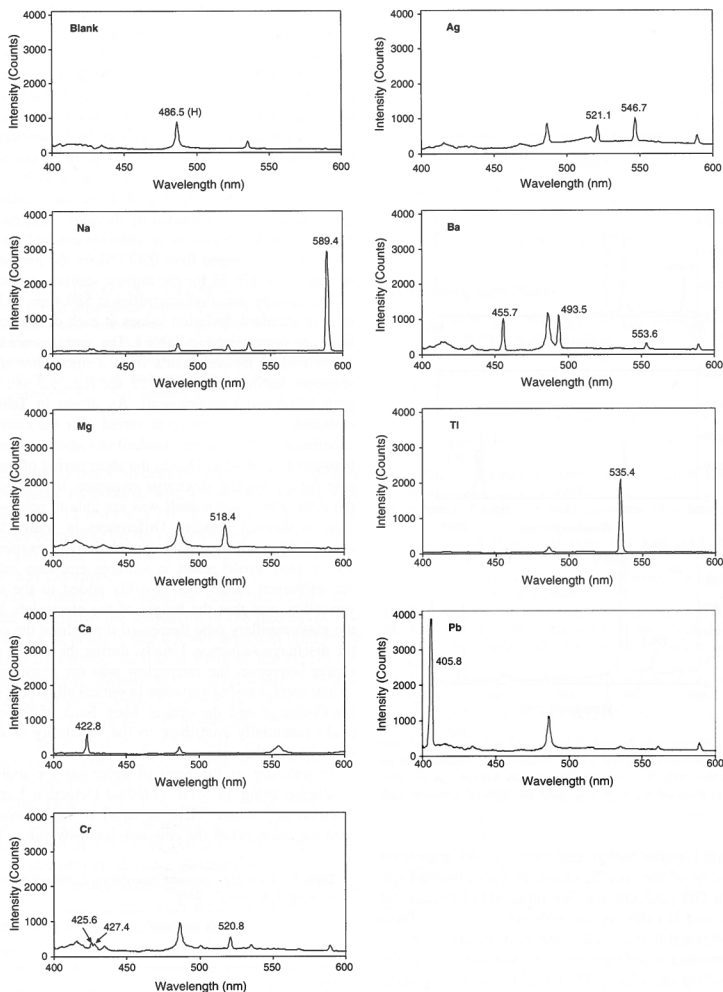


Figure 5. Emission spectra (400–600 nm) of selected environmentally relevant elements collected using the microglow discharge device described in this study. Selected emission lines are labeled.²⁷ A 2% nitric acid blank is included for reference.

for the wavelength range depicted. In general, significant background emission was observed between 280–390 nm (Figure 4), possibly limiting the usefulness of the open air microglow technique in this region. The analysis of Mn,

Fe, Co, Ni, and Cu would likely be problematic unless a reliable method for subtracting the background emission could be developed—efforts to subtract the background spectrum were not attempted in this study. Previous papers

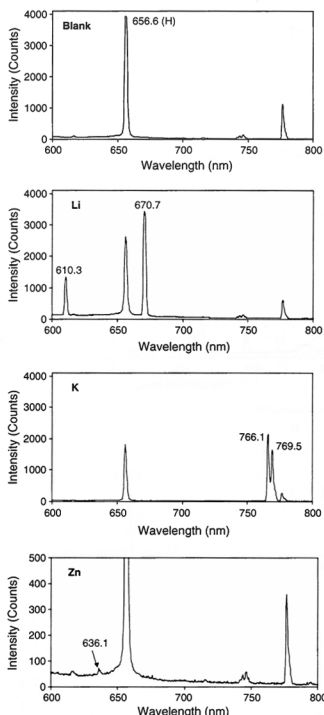


Figure 6. Emission spectra (600–800 nm) of selected environmentally relevant elements collected using the microglow discharge device described in this study. Selected emission lines are labeled.²⁷ A 2% nitric acid blank is included for reference. Note the reduced emission scale for Zn.

have reported similar background emission with microglow devices; some of the specific emission lines observed correspond to OH (283 nm and 306 nm), NH (336 nm), N₂⁺ (358 nm), and H (486 nm and 656 nm).^{2,3,5,8,11,14} These lines are denoted in the blank samples in Figures 4–6.

The remaining wavelength regions showed relatively few background emission lines. Therefore, the remaining metal analytes in Figures 4–6 have a good possibility for satisfactory determination due to minimal background interferences. One exception is Zn, which has only minimal sensitivity (note the reduced emission scale in Figure 6). As mentioned in the Introduction, a major advantage of atomic spectroscopy is the specificity of the technique. Interference from other elements (besides the background emission discussed above) is rare due to the narrow width

of the emission lines. In these rare instances where an interfering species is present, employing an alternate emission line can usually be used to overcome the problem.

Quantitative Determination of Sodium. A quantitative evaluation of the atmospheric pressure open-air microglow discharge atomic emission source was also conducted. The standard concentrations are given in the Experimental Section. The standards were analyzed at 589.4 nm using the microglow apparatus; all peak emissions were baseline corrected. It is worth repeating that the ionic character of the standards was dominated by the nitric acid matrix, not by the sodium, potassium, or chloride concentrations. The ionic strengths ranged from 0.475 M for the lowest sodium standard to 0.476 M for the highest sodium standard.

The average emission intensities at 589.4 nm and percent relative standard deviation values at each of the concentrations are summarized in Table I. The averages are based on 12 individual measurements from a microglow discharge sequence lasting a total of ~15 sec (i.e., 1.3 sec between each individual measurement). As shown in Table I, the emission intensities are quite varied over the course of an experiment—the relative standard deviation values ranged between 12 and 42%. Due to the short period of time available for a complete discharge sequence, it is possible that the microglow source itself was not able to achieve a high level of thermal stability. Differences in source temperature would result in variable populations of excited atoms, and in turn would result in variable emission intensities. An additional factor that possibly added to the emission variability was that the height of the electrolyte liquid in the glass capillary tube decreased throughout the course of the discharge sequence. Finally, during the course of a discharge sequence, the microglow was not consistent in its spatial form, causing variation in optical alignment between the discharge and the optical fiber. Each of these factors could potentially contribute to the variability in emission intensity for the sodium samples.

An estimate of the limit of detection for sodium was conducted using an MDL (Method Detection Limit) type calculation,²⁸ where MDL is equal to the absolute standard deviation (*s*) of the emission intensity values (in units

Table I. Microglow emission intensities (EI) and percent relative standard deviations (% RSD).

Conc. ^a	Not IS corrected ^b		K IS corrected ^c	
	EI	% RSD	EI	% RSD
0.1	160	31	29	6
0.5	141	12	36	6
1	399	13	70	9
5	1083	22	162	3
10	1130	16	325	5
50	1758	42	1078	15
100	2815	26	1458	18

^aSodium concentration in mg/L.

^bNa emission at 589.4 nm (baseline correction only).

^cIS corrected using K emission at 766.1 nm (also baseline corrected).

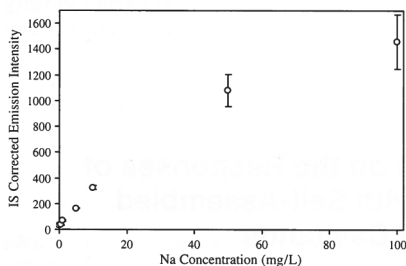


Figure 7. Sodium calibration curve obtained using the manual loading microglow discharge experimental setup with a potassium internal standard correction. Sodium emission was monitored at 589.4 nm; all emission values were baseline corrected. Emission intensities were corrected using the emission intensity of potassium at 766.1 nm (also baseline corrected) as an internal standard. Each data point is an average of 12 individual measurements. Error bars represent 95% confidence intervals; the error bars for data points below 50 mg/L are not discernible from the symbols.

of concentration) times Student's t value corresponding to 99% confidence (one-sided) with $n-1$ degrees of freedom; in all cases $n = 12$ and $t = 2.718$. The MDL-type detection limit varied depending on the concentration of sodium used for the calculation; however, a reasonable detection limit estimate was determined to be 0.17 mg/L using data from the 0.5 mg/L standard. It should be noted that efforts were not made to improve the sensitivity of the microglow discharge device. It is likely that a lower detection limit could be realized by varying the one or more of the experimental parameters (e.g., increasing the signal integration time, more rigidly fixing the optical components, etc.).

In an attempt to improve the quantitative determination of sodium, an internal standard correction was evaluated. The emission intensity due to sodium at 589.4 nm was corrected using the emission intensity due to potassium at 766.1 nm (both values were baseline corrected); these corrected values are also summarized in Table I. Potassium was added at a level of 100 mg/L to all standards. The potassium internal standard yielded more precise analyses (the relative standard deviation values ranged between 3 and 18%), even with the short time period over which the discharge occurs. A calibration curve using the potassium internal standard corrected sodium emission intensities was constructed. As expected, the emission intensities increase with increasing concentration, and the data are linear between 0.1 and 50 mg/L. However, deviation from linearity is observed at higher concentrations (see Figure 7). The detection limit using the 0.5 mg/L standard as above was calculated to be 0.08 mg/L using the potassium internal standard method. This is approximately a factor of two

lower than the detection limit calculated without the internal standard correction.

Acknowledgments: This work was funded by the University of Wisconsin Sea Grant Institute under grants from the National Sea Grant College Program, National Oceanic and Atmospheric Administration, U.S. Department of Commerce, and from the State of Wisconsin. Federal grant number NA16RG2257, project number R/MW85. The authors would like to thank Nathaniel A. Fillipan for assistance with the microglow experiments and Zachary Z. Brown for development of a data analysis software program.

References and Notes

1. L. S. Clesceri, A. E. Greenberg, and A. D. Eaton, *Standard Methods for the Examination of Water and Wastewater*, 20th Ed., American Public Health Association, Washington, DC (1998).
2. T. Cserfalvi, P. Mezei, and P. Apai, *J. Phys. D: Appl. Phys.* 12, 2184 (1993).
3. T. Cserfalvi and P. Mezei, *J. Anal. At. Spectrom.* 3, 345 (1994).
4. T. Cserfalvi and P. Mezei, *Fresenius J. Anal. Chem.* 7–8, 813 (1996).
5. P. Mezei, T. Cserfalvi, and M. Janossy, *J. Anal. At. Spectrom.* 10, 1203 (1997).
6. P. Mezei, T. Cserfalvi, M. Janossy, K. Szocs, and H. J. Kim, *J. Phys. D: Appl. Phys.* 20, 2818 (1998).
7. P. Mezei, T. Cserfalvi, and M. Janossy, *J. Phys. D: Appl. Phys.* 11, L41 (1998).
8. Y. S. Park, S. H. Ku, S. H. Hong, H. J. Kim, and E. H. Piepmeier, *Spectrochim. Acta B* 6–8, 1167 (1998).
9. H. J. Kim, J. H. Lee, M. Y. Kim, T. Cserfalvi, and P. Mezei, *Spectrochim. Acta B* 7, 823 (2000).
10. W. C. Davis and R. K. Marcus, *J. Anal. At. Spectrom.* 9, 931 (2001).
11. R. K. Marcus and W. C. Davis, *Anal. Chem.* 13, 2903 (2001).
12. P. Mezei, T. Cserfalvi, H. J. Kim, and M. A. Mottaleb, *Analyst* 5, 712 (2001).
13. M. A. Mottaleb, Y. A. Woo, and H. J. Kim, *Microchem. J.* 3, 219 (2001).
14. C. G. Wilson and Y. B. Gianchandani, *IEEE T. Electron. Dev.* 12, 2317 (2002).
15. G. Jenkins and A. Manz, *J. Microchem. Microeng.* 5, N19 (2002).
16. M. A. Mottaleb, J. S. Yang, and H. J. Kim, *Appl. Spectrosc. Rev.* 3, 247 (2002).
17. L. Que, C. G. Wilson, J. A. Esclafar de La Rode, and Y. B. Gianchandani, *IEEE International Conference on Solid-State Sensors and Actuators* (2003).
18. T. Cserfalvi and P. Mezei, *J. Anal. At. Spectrom.* 6, 596 (2003).
19. J. C. T. Eijkel, H. Stoeri, and A. Manz, *Anal. Chem.* 14, 2600 (1999).
20. J. C. T. Eijkel, H. Stoeri, and A. Manz, *Anal. Chem.* 11, 2547 (2000).
21. J. C. T. Eijkel, H. Stoeri, and A. Manz, *J. Anal. At. Spectrom.* 3, 297 (2000).
22. Z. Jin, Y. Su, and Y. Duan, *Anal. Chem.* 2, 360 (2001).
23. F. G. Bessoth, O. P. Naji, J. C. T. Eijkel, and A. Manz, *J. Anal. At. Spectrom.* 8, 794 (2002).
24. J. A. Hopwood, *J. Microelectromech. S.* 3, 309 (2000).
25. C. G. Wilson and Y. B. Gianchandani, *J. Microelectromech. S.* 1, 50 (2001).
26. W. C. Davis, D. Strand, and R. K. Marcus, *Am. Lab.* 9, 28 (2003).
27. *CRC Practical Handbook of Spectroscopy*, CRC Press, Boca Raton, FL (1991).
28. U.S.EPA, *Fed. Regist.* 209, 43430 (1984).