C. *Appl. Phys. Lett.* **1992**, *60*, 639.
11. Jung, K. H.; Shih, S.; Kwong, D. L. *J. Electrochem. Soc.* **1993**, *140*, 3046.
12. Perora-Koch, V.; Muschik, T.; Kux, A.; Meyer, B. K.; F. Koch.; Lehmann, V. *Appl. Phys. Lett.* **1992**, *61*, 943.
13. Nishitani, H.; Nakata, H.; Fujiwara, Y.; Ohyama, T. *Jpn. J. Appl. Phys.* **1992**, *31*, L1577.
14. LT, Q.-S.; Fang, R.-C.; in *Porous Silicon*; ed. by Feng, Z. C.; Tsu, R. World Scientific, Singapore, 1994; pp 235.
15. Lee, C.-W.; Oh, M.-K.; Jang, J.-M. *Langmuir* **1993**, *9*, 1934.
16. Lauehaas, J. M.; Credo, G. M.; Heinrich, J. L. Sailor, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1514.
17. Chun, J. K. M.; Bocarsly, A. B.; Cottrell, T. R.; Benziger, J. B.; Yee, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 3024.
18. Sheen, C. W.; Shi, J.-X.; Martensson, J.; Parikh, A. N.; Allara, D. L. *J. Am. Chem. Soc.* **1992**, *114*, 1514.
19. Guy, Y.; Lin, R. A.; Smentkowski, V. S.; Waldeck, D. H. *Langmuir*, **1995**, *11*, 1849.
20. Lingord, M. R.; Chidsey, C. E. D. *J. Am Chem. Soc.* **1993**, *115*, 12631.
21. Brown, T. G.; Bradfield, P. L.; Hall, D. G. *Appl. Phys. Lett.* **1987**, *51*, 1585.
22. Bakhadyrkhanov, M. K.; Kurbanova, U. K. *Semiconductor* **1994**, *28*, 739.
23. Corpenter, M. S.; Melloch, M. R.; Lundstrom, M. S.; Tobin, S. P. *Appl. Phys. Lett.* **1988**, *52*, 2157.
24. Hwang, K. G.; Li, S. S. *J. Appl. Phys.* **1990**, *67*, 2162.
25. Lee, H. H.; Racicot, R. J.; Lee, S. H. *Appl. Phys. Lett.* **1989**, *54*, 724.
26. Lunt, S. R.; Santangelo, P. G.; Lewis, N. S. *J. Vac. Sci. Technol., B* **1991**, *9*, 2333.
27. Bain, C. D. Troughton, E. B.; Tao, Y-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.
28. Feng, Z. C.; Wee, A. T. S.; Tan, K. L. *J. Phys. D*, **1994**, *27*, 1968 and references therein.
29. Wagnerr, C. D. *Handbook of X-Ray Photoelectron Spectroscopy*; Perkin-Elmer, Minnesota, U.S.A. 1979; p 184.
30. Laiho, R.; Pavlov, A. *Phys. Rev., B* **1995**, *51*, 14774.
31. Buda, F.; Kohanoff, J.; Parrinello, M. *Phys. Rev. Lett.* **1992**, *69*, 1272.

A Study of Laminar Flow Torch in Microwave Induced Plasma Atomic Emission Spectrometry

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A comparative study of different torches in the Microwave Induced Plasma is reported. Three types of torches that have been used in this area are characterized and compared with each other. Especially, recently developed laminar flow torches have been optimized in design and analytical performances. The ratio of inner to outer tubes is found to be the most important parameter. As inner tube size increases, recirculating region also increases and consequently, sensitivity becomes better. An optimized laminar flow torch has been coupled to a gas chromatography and examined for halogen compounds. Detection limits are 25 pg s^{-1} for Cl and 12 pg s^{-1} for Br. These values are improved over the conventional laminar flow torch.

Introduction

Helium Microwave Induced Plasma (He MIP) has been developed as an element-selective emission detector for Gas Chromatography (GC) and the system has been widely studied by various researchers.[1~7] In his first paper of GC-MIP, Beenakker[8] employed simple straight capillary quartz tubes of which diameter ranging from 0.5 to 3.0 mm. The sensitivities reported were in pg s^{-1} range. However, the plasma tube, capillary flow torch (CFT), frequently suffered from problems such as memory effect, etching of the inner surface of the plasma tube, and wandering of plasma inside the torch. To reduce these problems, Bollo-Kamara[9] designed a Tangential Flow Torch (TFT) which forced plasma gas to flow through a specially designed glass centersert. Much like a torch of ICP, TFT could provide a self-centered plasma inside the torch. Plasma did not touch the wall and showed no etching problem. Several workers[10~13] used TFT in the MIP study with some successes. However, due to a large amount of plasma gas employed (2-10 L/min) for TFT, the sample residence time and consequently, sensitivity is significantly sacrificed.

A recent development in the area of torch design was reported by Bruce *et al.*[14,15] who employed a laminar flow torch (LFT). A stable plasma was formed by laminar flow of gas, creating a recirculating region separated from the main gas stream. They showed much improvement of detection limits for Cl and Br compared to TFT. When compared to CFT, LFT showed better stability and longer life time. The torch required a water-cooled cavity and was operated

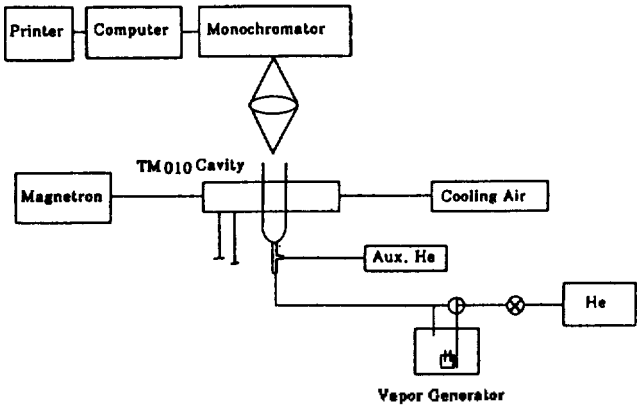

Figure 1. A block diagram of the experimental system.

Table 1. Instruments and operating Conditoins

Microwave generater:	2.45 GHz Model MPGA4 (Opthos Company) 120W
Cavity:	Modified TM_{010} (double tuned)
MC:	PE Model 5000 Czerny-Tuner Type, Focal length: 0.4 m, D^{-1} (1.3 mm/mm)
PMT:	Hamamatsu E717-07
Lenz:	Focal length 13 cm, Diameter 4 cm
Spectral Width:	0.04 nm
Vapor Generator System:	Lab. built
Gas Chromatograph:	Hewlett Packard 5890A
Oven Temp (℃):	130-160
Column:	Carbowax 20M
Carrier gas:	Helium (30-60 mL/min)

at less than 100 mL min^{-1} of helium gas. Fielden *et al.*[16] also used a laminar flow torch and optimized it for GC. The parameters they investigated were sheathing gas flow rate, insertion depth, and forward power.

However, there is a great need to investigate on the LFT design. Especially, the most important parameter that should be studied in laminar flow torch design is the ratio of inner to outer tube diameter. The ratio of the outer diameter of an inner tube to the inner diameter of an outer tube (R) is critical because it affects Reynolds number, which indicates whether the flow is laminar or turbulent. In addition to that, the sample residence time will be dependant upon the R values. Larger R values can create a larger recirculating region and increase the sensitivity due to the increased sample residence time. The purpose of this research is to study three different types of torches (CFT, TFT, LFT) and to examine their characteristics as well as their practicality. Since LFT has shown the best analytical performances among the three, LFT has been selected and studied in detail. Different designs of LFT are examined and optimized. Sensitivity and analytical characteristics are studied for different values of R. Improved detection limits are found over the conventional laminar flow torch for Cl and Br containing compounds.

Experimental

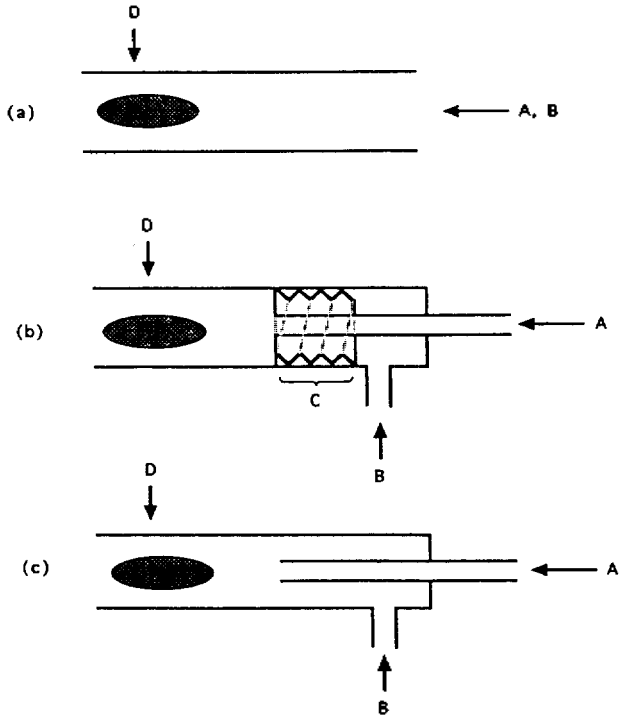

Figure 2. Schematic diagram of three MIP discharge tubes. a) capillary flow torch, b) tangential flow torch, c) laminar flow torch; A) sample gas, B) plasma gas, C) threaded area, D) plasma discharge region.

Instrumentation. A block diagram of the experimental system is shown in Figure 1. The instruments and their operating conditions are summarized in Table 1. The plasma was supported in a modified Beenakker cavity. Microwave power was supplied by a 2450 MHz generator. Both forward and reflected power was measured by the meter installed in front of the generator. The image of plasma was focused onto the entrance slit of the monochromator. Sample introduction into the torch was achieved by either a vapor generator or a GC. For the CFT, swagelok "T" connector and a valve were used to adopt the make-up gas which was necessary to sustain the plasma.

Capillary Flow Torch used in this experiment is a simple, open quartz tube with 6.0 mm o.d. and 2.0 mm i.d. Tangential flow torch has been constructed according to Bollo-Kamara's design.[9] However, in this experiment, the tangential insert part is made of PTFE. The detailed description of the design is given in elsewhere.[17] A schematic diagram of three torches is shown in Figure 2. The Laminar Flow Torch is made of two concentric tubes as shown in Figure 3. Sample is introduced through the center tube and the plasma gas is introduced through the outer tube. The size of outer tube used is 2 mm or 3 mm i.d. with 6 mm o.d. The o.d. of inner tube has been varied from 1.0-2.0 mm. Since the outer tube is relatively small, it is rather difficult to make the torch concentric. To ease the centering of the inner tube, adjusting screws[15] are used as shown in Figure 3.

GC and the vapor generating system. A Hewlett-Packard Gas Chromatography with a 1/8 in. o.d.×8-ft-long stainless steel packed column coated by 2% OV-1 stationary

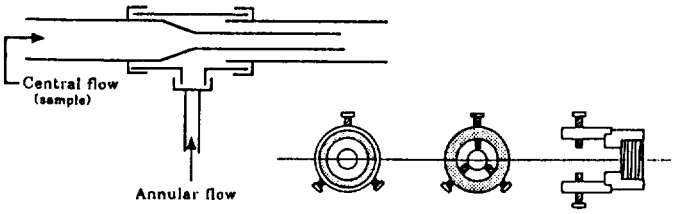

Figure 3. Flow design of LFT and centering apparatus.

Table 2. Comparison of Three Types of Torches used in MIP system

	TFT	LFT	CFT
Plasma gas flow rate (L/min)	1.2-5.0	~0.2	>0.1
Torch o.d.		6.0	
Torch i.d. (mm)	5.0	2.0-3.0	2.0
Stability	good	good	poor
Detection Limit* Cl (pg/s)	41.5	8.0	0.5*

The vapor generation system is used. *Calculated values using the equation proposed by reference 18

phase was used throughout the experiment. The injector temperature was maintained at 140-160 ℃ with the oven temperature kept at 80-130 ℃. The He carrier gas flow rate was 30-60 mL min^{-1}. To prevent condensation of the sample, connective tubing was heated using heating tapes with the temperature being controlled by a variac.

Sample also could be conveniently introduced by using a vapor generator instead of a GC. The vapor generator system utilize the effusion phenomenon and it could provide a constant sample input. A small leaking vial (diffusion tube) which contains a sample to be analysed is put into a rather small flask so that the sample could leak out slowly. Helium is then passed unto the diffusion tube. Though the concentration is difficult to be known exactly, the generator can provide a constant concentration under the constant temperature, diffusion path length, and pressure. Practically, for a given apparatus, a constant flow rate over the liquid sample will result a constant concentration of sample.

Result and Discussion

Comparison of three types of torches. Experimental conditions and the performances of three types of torches are compared in Table 2. In addition to sample carrier gas, plasma gas flow rate is also an important parameter since it keeps the plasma at the center of the torch. The plasma gas flow rate should be increased when a higher power is employed. Usually, CFT gives the best detection limit because it gives good interaction of the sample with the plasma and consumes the least amount of plasma gas. But in terms of stability, CFT is not a good choice. The analytical performance deteriorates fast with time. TFT shows good stability and produces a stable plasma. But the torch is fairly difficult to construct and more importantly, analytical sensitivity is poor. Considering performance and stability, LFT shows the best performance and has been used throughout the experiment. The detection limit is obtained when the signal is three times larger than that of background while sample is fed from the vapor generator or GC. The area of the peak obtained is determined by multiplying the peak height by the width of the peak at one-half the peak height. The area of noise is determined measuring the height of the background noise and multiplying this by the peak width. The ratio of signal-to-noise areas is related to the amount of sample injected. The diffusion rate of analyte vapor is determined according to the equation proposed by Altshuller and Cohen.[18] Thus, the detection limit could be different when GC is used. Nonetheless, the trend should be the same regardless of the sample introduction system.

Table 3. The Detection Limit of the Laminar Flow Torch in GC unit: pg/s

	Cl (479.5 nm)	Br (470.5 nm)
Normal Condition (R=0.5)	25	71
High Sensitivity (R=0.8-0.95)	12	25
The Vapor Generator*	8	8
Bruce *et al.*[14]	40	62

Detection Limit is determined based on 3σ. *The vapor generating system is used.

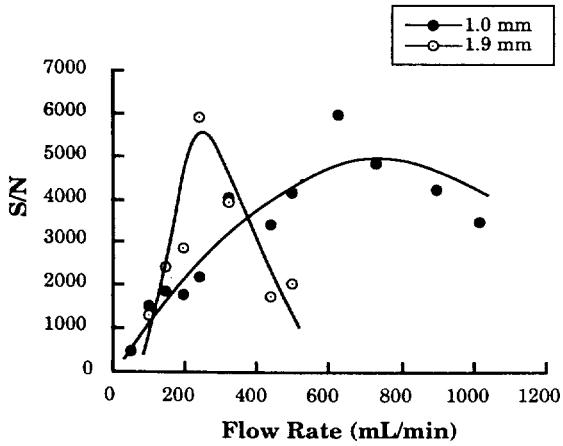

Figure 4. Optimization of plasma gas flow rate for 2 mm LFT. Inner tubes are 1.0 mm (●) and 1.9 mm (○).

Optimization of LFT. The plasma gas flow can affect both plasma itself and its analytical performances most significantly. S/N changes with the plasma gas flow for different torch sizes are shown in Figure 4 and Figure 5. Power (120 W) and sample gas flow rate are fixed and only plasma gas flow rate is varied. Figure 4 shows about 2 mm i.d. outer tube. Two sizes of inner tubes are used (1.0 mm and 1.9 mm o.d). Figure 5 shows about 3 mm i.d. outer tube. Also, two sizes of inner tubes (1.0 mm and 2.0 mm o.d.) are used.

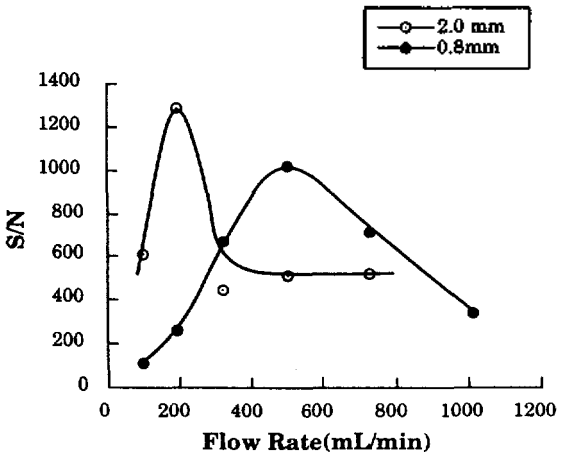

Figure 5. Optimization of plasma gas flow rate for 3 mm LFT. Inner tubes are 0.8 mm (●) and 2.0 mm (○).

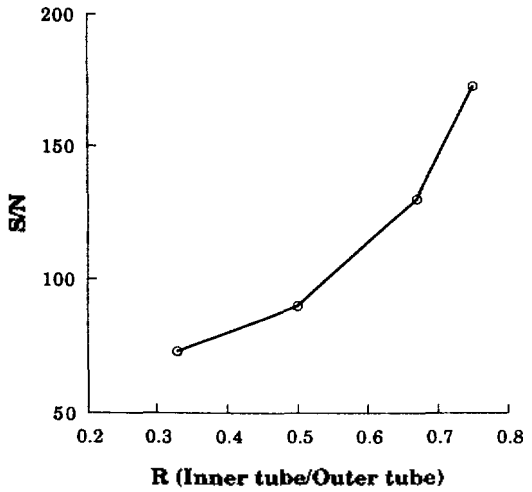

Figure 6. Changes of S/N of Cl with different sizes of the inner tube to outer tube in LFT.

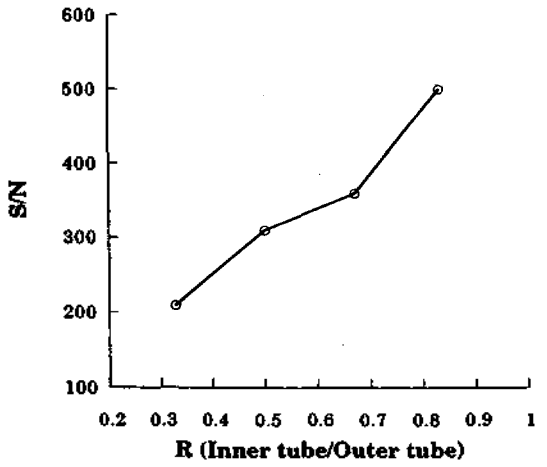

Figure 7. Changes of S/N of Br with different sizes of the inner tube to outer tube in LFT.

Regardless of the sizes, all of them shows the maximum S/N at a certain flow rate.

At low flow rates, deposition of pyrolysis product occurs on the inner wall of outer torch. These products can cause plasma to wander around inside the torch and consequently, decrease sensitivity. The product can not be easily removed by acids or heating. At higher flow rates, the rate of deposition decreased and the stability of plasma improved. However, after a certain range, S/N decreases because that the plasma is cooled and the sample residence time is reduced. When the R value (the ratio of inner tube to outer tube) is increased (1.9 mm in Figure 4 and 2.0 mm in Figure 5), the optimum flow rate range is narrowed. As the inner tube gets larger for a fixed size of outer tube, apparently, the gas flow becomes more critical. The gas flow could become turbulent easily for a larger inner tube because the gap between the two concentric tubes is narrowed. Thus, the optimum flow range is narrowed. Generally, higher gas flow rates create more of eddy flow at the tip of the inner tube and consequently, increase the residence time of sample. S/N is increased with the flow rate accordingly. At higher flow rates, plasma can be cooled and the sample residence time decreases due to high plasma gas velocity. Eventually, the flow becomes turbulent and S/N decreases also. This type of behavior is more apparent for a large inner tube. On the other hand, a small inner tube is less sensitive to gas flow rates and responds slowly.

Positional effect of LFT with respect to the cavity is considered. By moving the LFT inside the cavity, the plasma formation is changed. Fielden *et al.*[16] reported that S/N was the best when the inner tube protruded halfway into the cavity. Plasma was formed in the open region of the torch as well as in the inner tube. However, in our study, S/N became worse when the centersert contacted with the plasma. When the distance between the tip of the inner tube and plasma is too close, plasma becomes unstable. On the other hand, when the distance is too far, sample is easily mixed with the plasma gas before it contacts with the plasma and consequently, S/N decreases. It is found to be the best when the distance between the tip of the inner tube and plasma is about 2 mm.

The ratio of inner-to-outer tube size (R) is very critical in forming the eddy flow for the LFT. R is varied from 1/2 to 1 meaning that outer diameter of centersert is about one-half the diameter of outer tube to nearly equal to it. Figure 6 and Figure 7 are showing S/N changes for different sizes of inner tube for Cl and Br compounds, respectively. As expected, S/N increases with R values. Interestingly, signal is increasing but noise is increasing even more rapidly. This can be explained by following reasons. First, the deposition of carbon ("carbonizing") on the wall of the outer tube become significant. Furthermore, it becomes more difficult to align the torches concentric. Even a little asymmetry can cause a large turbulence of gas flow. It is almost impractical to make a LFT of which R is close to 1. Though S/N is expected to be better, it is not a trivial thing to make several torches having large R values yet behaving in the same way. Another point that should be considered about R is resolution. LFT with a large R gives good sensitivity by creating a recirculating region at the tip of the inner tube, and increases the sample residence time. However, if samples stay

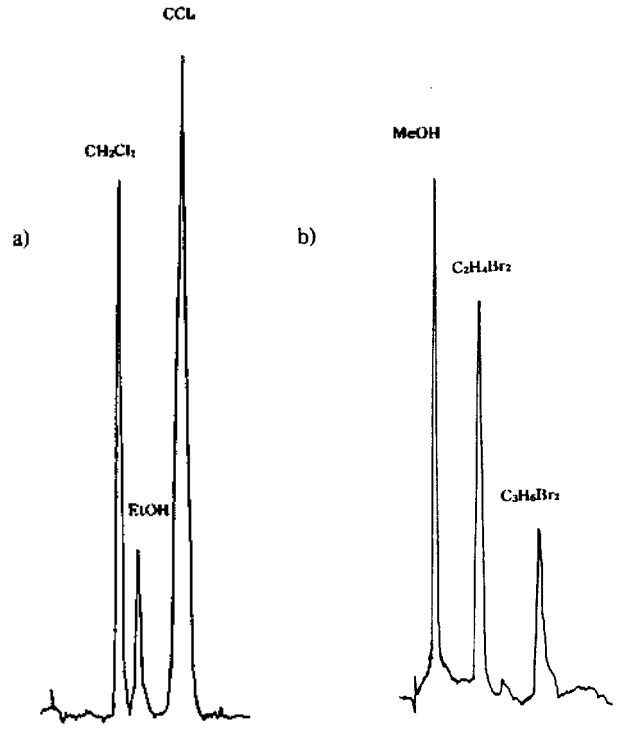

Figure 8. GC chromatograms of Cl and Br containg compounds; a) contains CH_2Cl_2 and CCl_4 in EtOH b) contains $C_2H_4Br_2$ and $C_3H_6Br_2$ in MeOH.

in the region too long, resolution is worsened. Thus, too large R values are avoided. In the real experiments, R of 0.5-0.8 is found to be good compromising value. However, if sensitivity is considered over resolution, higher R values can be used.

Gas Chromatography Studies. An optimized LFT of which R value is 0.8 has been interfaced to a packed column gas chromatography and the preliminary study has been performed to evaluate the performance of the MIP system as an element specific detector. Figure 8 shows that all chlorine and bromine compounds could be detected well. The solvent also shows some peak intensity due to the change of spectral background. Usually, the selectivity is large enough to distinguish a peak from solvent or noise. In order to correct a spectral background, an oscillating quartz plate[19] behind the entrance slit can be employed. Another approach to eliminate background is using a photo-diode array.

The detection limits were determined for the optimized LFT for Cl and Br. 0.02 μL of sample was injected to the GC system. They are compared to the one reported earlier by Bruce *et al.*[14] and the values are comparable for Br or better in case of Cl. However, in this study, straight inner tubes are used instead of a bell shaped one employed by them. The advantage of using a straight inner tube is easy of production, and increased resolution in GC peaks. In Bruce's work, the recirculating region is larger and resolution can be deteriorated significantly. The optimized torch in this study shows similar or better detection limit, yet not sacrificing resolution severely.

Acknowledgment. The authors wish to express gratitude for the financial support by the Korea Science and Engineering Foundation. (94-0800-03-02).

References

1. McCormack, A. J.; Tong, S. C.; Cooke, W. D. *Anal. Chem.* **1965**, *37*, 1470.
2. Bache, C. A.; Lisk, D. J. *Anal. Chem.* **1965**, *37*, 1477.
3. Estes, S. A.; Uden, P. C.; Barnes, R. M. *Anal. Chem.* **1981**, *53*, 1829.
4. Goode, S. R.; Chambers, B.; Budin, N. P. *Appl. Spectrosc.* **1983**, *37*, 439.
5. Quimby, B. D.; Sullivan, J. M. *Anal. Chem.* **1990**, *62*, 1027.
6. Brenner, K. S. *J. Chromatogr.* **1978**, *167*, 365.
7. Wasik, S. P.; Schwarz, I. P. *J. Chromatogr. Sci.* **1980**, *18*, 660.
8. Beenakker, C. I. M. *Spectrochim. Acta* **1977**, *32B*, 173.
9. Bollo-Kamara, A.; Codding, E. G. *Spectrochim. Acta* **1981**, *36B*, 973.
10. Michlewicz, K. Z.; Caranhan, J. W. *Anal. Chem.* **1986**, *58*, 3122.
11. Michlewicz, K. Z.; Caranhan, J. W. *Anal. Chim. Acta* **1986**, *183*, 275.
12. Haas, D. L.; Caruso, J. A. *Anal. Chem.* **1985**, *57*, 846.
13. Deutsch, R. D.; Hieftje, G. M. *Appl. Spectrosc.* **1985**, *39*, 214.
14. Bruce, M. L.; Workman, J. A.; Caruso, J. A.; Lahti, D. L. *Appl. Spectrosc.* **1985**, *39*, 935.
15. Bruce, M. L.; Caruso, J. A. *Appl. Spectrosc.* **1985**, *39*, 942.
16. Fielden, P. R.; Jiang, M.; Snook, R. D. *Appl. Spectrosc.* **1989**, *43*, 1444.
17. Pak, Y. N.; Koirtyohann, S. R. *Appl. Spectrosc.* **1991**, *45*, 1132.
18. Altshuller, A. P.; Cohen, I. R. *Anal. Chem.* **1960**, *32*, 802.
19. Kirkbright, G. F.; Snook, R. D. *Appl. Spectrosc.* **1983**, *37*, 11.