IS-T-1811

Calibration of Laser Ablation Inductively Coupled Plasma Mass Spectrometry using Dried Solution Aerosols for the Quantitative Analysis of Solid Samples

by

Leach, James

MS Thesis submitted to Iowa State University

RECEIVED
MAY 20 1999
OSTI

Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011

Date Transmitted: February 12, 1999

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY

UNDER CONTRACT NO. W-7405-Eng-82.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

AVAILABILITY:

To DOE and DOE contractors: Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

prices available from: (615) 576-8401
FTS: 626-8401

To the public: National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

This thesis is dedicated to the loving memory of Maxine Roselyn Leach

TABLE OF CONTENTS

CHAPTER 1. GENERAL INTRODUCTION

* Preprint

* Removed for separate processing —

CHAPTER 1. GENERAL INTRODUCTION

Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) has become the method of choice for elemental and isotopic analysis.[1,2] Several factors contribute to its success. Modern instruments are capable of routine analysis at part per trillion levels with relative detection limits in part per quadrillion levels. Sensitivities in these instruments can be as high as 200 million counts per second per part per million with linear dynamic ranges up to eight orders of magnitude. With standards for only a few elements, rapid semiquantitative analysis of over 70 elements in an individual sample can be performed.[3]

Less than 20 years after its inception[4] ICP-MS has shown to be applicable to several areas of science. These include geochemistry,[5-7] the nuclear industry,[8-10] environmental chemistry,[11-13] clinical chemistry,[14,15] the semiconductor industry,[16-19] and forensic chemistry.[20,21]

In this introduction, the general attributes of ICP-MS will be discussed in terms of instrumentation and sample introduction. The advantages and disadvantages of current systems are presented. A detailed description of one method of sample introduction, laser ablation, is given.

ICP-MS Instrumentation

The basic design of all ICP-mass spectrometers includes three main components: the ICP, the ion extraction and focusing optics, and the mass analyzer and detector. A brief description of each is given below.

The ICP, shown in Figure 1, is an atmospheric pressure electrical discharge sustained in an atmosphere of an inert gas, typically argon (Ar). Radio-frequency (RF) energy is supplied to the plasma through a series of water-cooled copper loops known as the load coil. The RF power operates at one of two frequencies, 27.12 or 40.68 MHz, and at powers between 650-1500 watts[22]. The load coil surrounds a quartz torch, which consists of three concentric tubes through which the argon gas is introduced to the plasma. The outermost tube supplies the largest flow of Ar at approximately 15-16 L/min., and is commonly called the coolant, outer, or plasma gas flow. The middle tube supplies what is known as the auxiliary gas. This flow rate varies considerably but typically operates at or just above 1 L/min. Sample is introduced to the plasma through the innermost tube by the supply known as the nebulizer or aerosol gas. This flow punches a hole or "central channel" through the center of the plasma. Typical flow rates for this supply are around 1 L/min.

Once the plasma is initiated, RF energy from the load coil is directly coupled into the induction region. The temperature in this region is believed to possibly reach 10 000 K. The gas in the central channel is heated mainly by conduction and by radiation from the induction region, and is probably between 5000 K and 7000 K.[3] In this manner the analyte, which flows into the induction region through the central channel, is ionized indirectly by the plasma. As the analyte droplets pass through the central channel they undergo the following processes: desolvation, dissociation, atomization, ionization, and excitation. The ions produced are predominantly singly-charged.

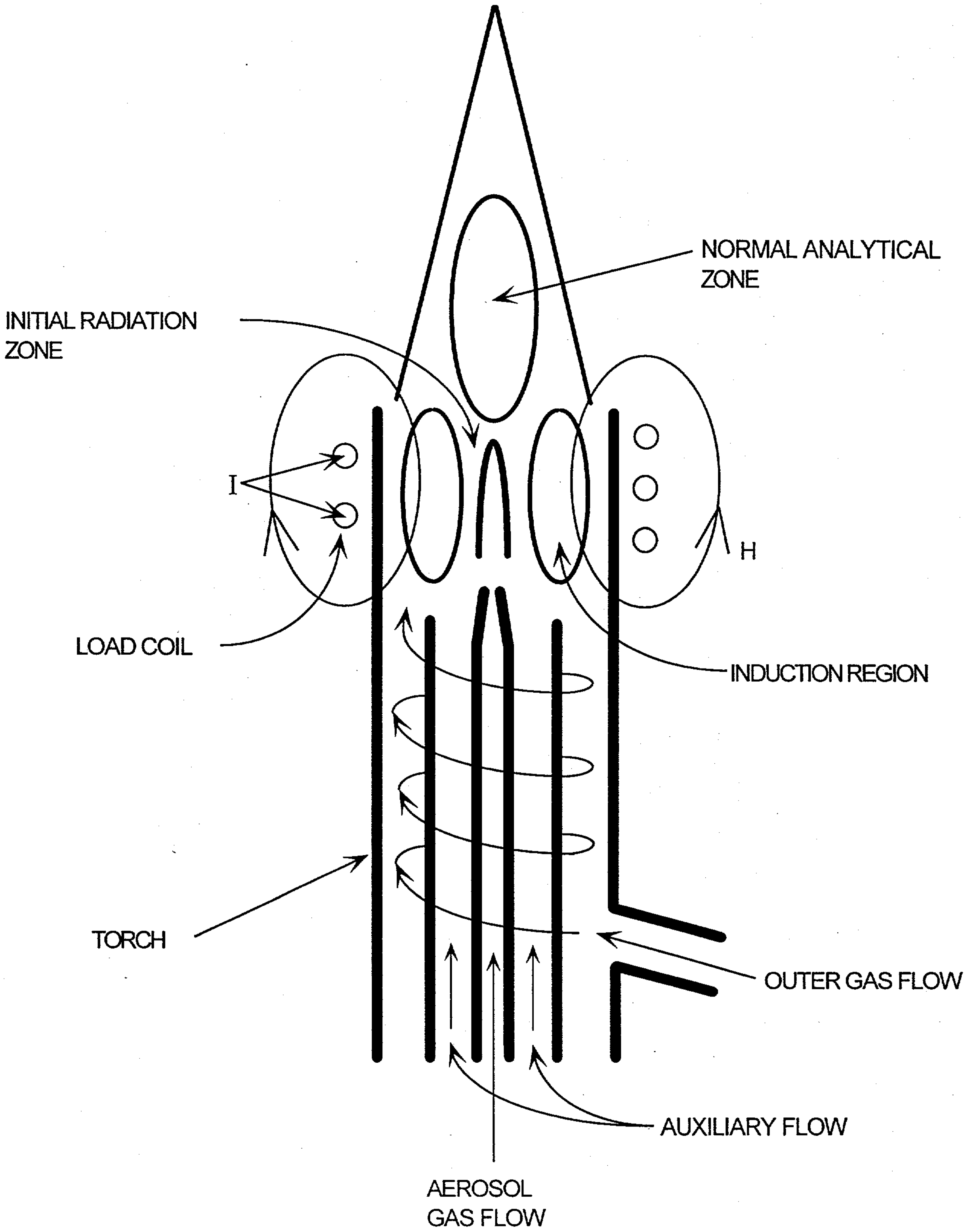

Figure 1. Diagram of the ICP.

Ions are produced at atmospheric pressure by the ICP, and mass spectrometers must operate under vacuum, thus necessitating a system of differential pumping. Typical ICP-mass spectrometers have three stages of pumping. Such a system is shown in Figure 2. The first stage of pumping exists between the sampler and skimmer cones, and typically operates at or just above 1 torr. The second stage is the region between the skimmer cone and the differential pumping orifice which contains the extraction lens and other ion optics, and operates at about 10^{-4} torr. The third stage contains further ion optics, the mass analyzer, and the detector, and typically operates at around 10^{-6} torr.

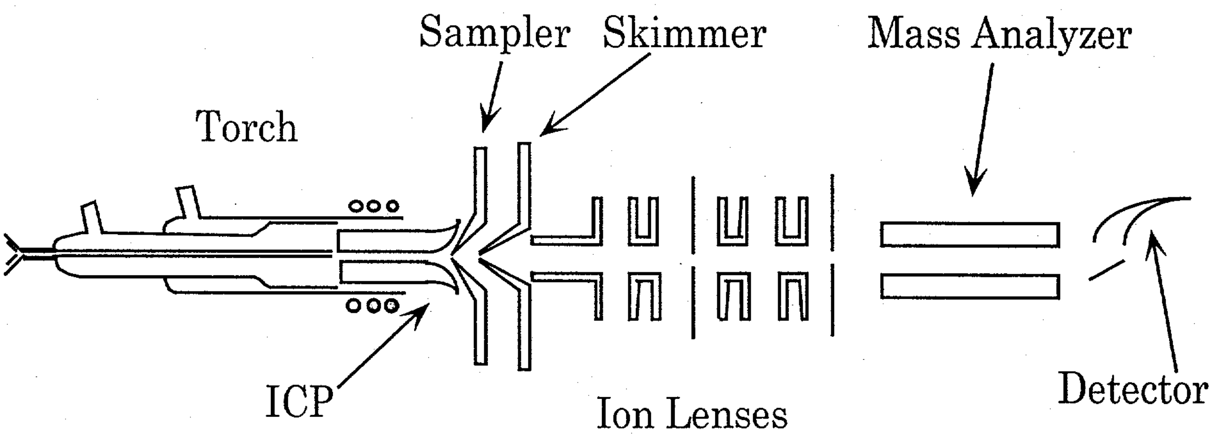

Figure 2. Components of a typical ICP-MS.

The plasma is quasineutral, that is, the number of positive ions and electrons are approximately equal. Ions from the plasma are first extracted through the sampling cone, which is immersed in the plasma. As it passes through the sampler, the ion beam expands supersonically. The ion beam is further extracted through the skimmer cone, whose tip protrudes into the collision-free region of the supersonic expansion. As the particles enter the extraction lens, the lighter and more mobile electrons are eliminated, leaving an ion beam consisting almost exclusively of positive ions. A detailed review of the ion extraction process is provided elsewhere.[24] The surviving ions are focused into the remaining ion optics and into the mass analyzer.

As shown in the next section, several types of mass spectrometers have been employed for use with the ICP. Each employs a different method for the differentiation of ions for subsequent detection. A review of the applications of each would be beyond the scope of this introduction; suffice to say each has its advantages and disadvantages.

The ions that successfully traverse the mass analyzer are detected by one of a number of ion detection devices. Briefly, the detector produces a signal which is directly proportional to the amount of ions impacting the detector per a given time. This signal can then be further manipulated for data analysis.

Twin-Quadrupole ICP-MS

Many kinds of mass spectrometers have been coupled with the ICP, including the quadrupole,[4-16,18-21] time-of-flight,[25-28] magnetic sector,[29,30] ion trap,[31-34] and ion cyclotron resonance.[35] The quadrupole is by far the most common, however, because it is rugged, easy to operate, compact, and relatively inexpensive.

The quadrupole mass filter operates by applying a combination of DC and RF potentials to four long rods. The RF and DC voltages and RF frequency are selected such that ions of only one *m/z* value traverse the rods un-filtered. In this fashion, the quadrupole acts as a *dynamic* mass filter as opposed to a static one.[36]

The major source of noise in ICP-MS is flicker noise, which contributes to poor precision in isotope ratio measurements. Since ions can be measured at only one *m/z* at a time, the quadrupole must hop back-and-forth between the isotopes of interest to perform isotope ratio measurements. This "peak-hopping" can limit the signal per *m/z* and introduce shot noise, which further reduces the precision. Transient signals such as laser ablation and chromatographic peaks can further exacerbate the problem. Simultaneous detection of signals by ICP emission spectroscopy[37,38] and multicollector MS[30] has been shown to greatly reduce flicker noise. It was proposed that simultaneous detection using the quadrupole would achieve the same result, while being much less bulky and expensive than multicollector instrumentation.

Such a device was constructed in this research group, largely by A.R. Warren and L.A. Allen, and is shown in Figure 3. Results showed that flicker noise is reduced to almost the counting statistics limit, allowing isotope ratio measurements to be performed with equal or better precision than virtually all single-quadrupole instruments. Moreover, unlike the multicollector devices, which are based on magnetic sector technology, the twin-quadrupole instrument is able to monitor signals of very different mass.[39-42]

Sample Introduction

Although samples can be introduced to the ICP in liquid, solid, or gaseous forms, by far the most common is aqueous solution.[3] To aid in its reduction to atomic ions in the ICP, the bulk liquid must first be reduced to small droplets. This is achieved through the use of a device known as a nebulizer. Nebulizers work basically by shattering the large liquid drops

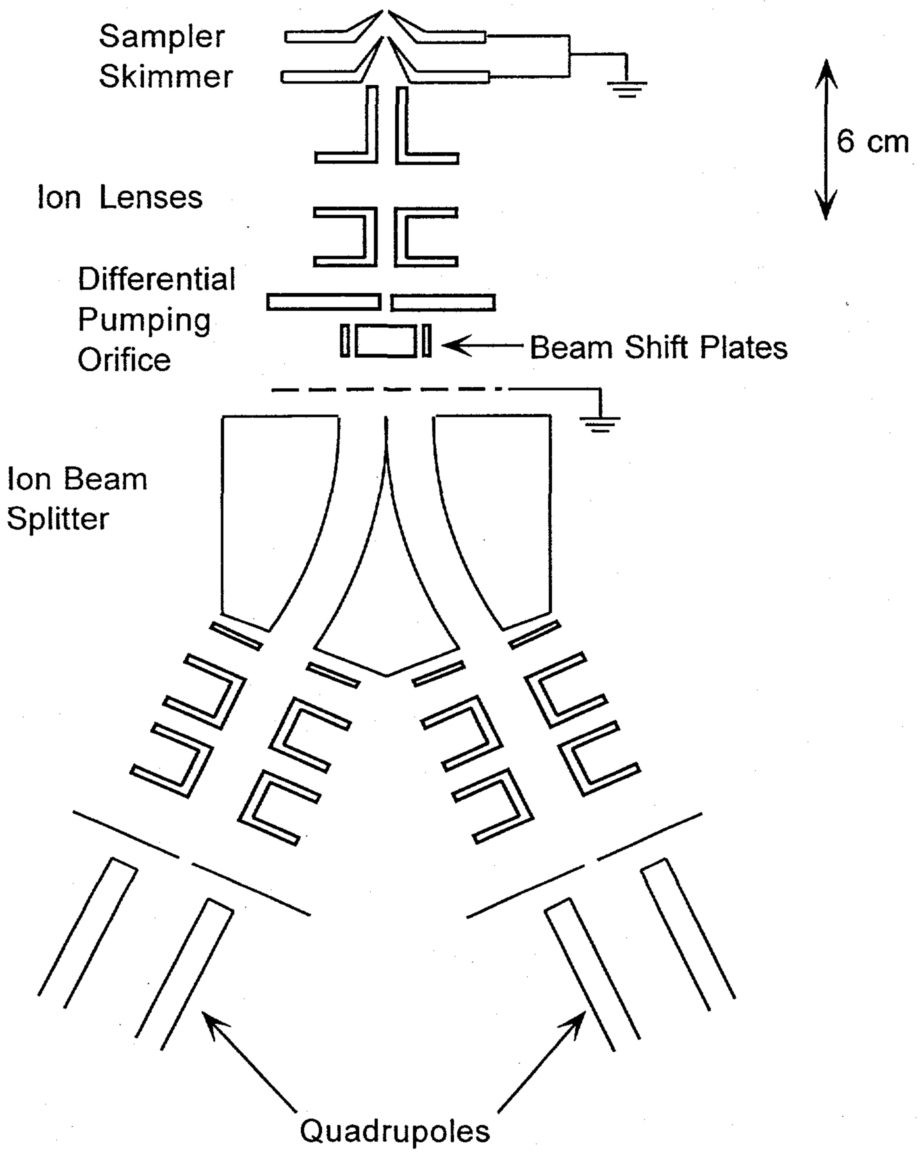

Figure 3. Diagram of the twin-quadrupole ICP-MS.

by vibration or gas flow into a fine mist of droplets, where they are swept by an argon stream through a spray chamber and then to the ICP. Several kinds of solution introduction devices have been employed for use with ICP spectrometry; pneumatic and ultrasonic nebulizers are the most common.[43]

Because ICP-MS is well suited for the analysis of solutions, solids are typically dissolved prior to analysis. Often however, direct analysis of solids is preferred to digestion for a number of reasons. Sample or surface inhomogeneity may be of concern,[21] the sampling depth of a surface may be of interest,[44] dissolution procedures can be time-consuming and run the risk of introducing contamination, and some samples, such as glasses and ceramics, simply do not dissolve. The method that has shown the most promise for the direct analysis of solids by ICP-MS is laser ablation.[45]

Laser Ablation

Laser ablation is loosely defined as the use of a high-powered laser to vaporize a portion of a solid sample for subsequent analysis by external instrumentation. When focused to a few square micrometers, pulsed laser beams can achieve power densities in excess of 10^{10} W/cm^2.(46) Power densities of this magnitude are sufficient to create what is known as a "laser-induced plasma". This micro-plasma generates enough heat to cause instantaneous heating of the surface of the material above the vaporization temperature (T_{vap}). Because heat dissipation is slow relative to the pulse duration, the underlying material also exceeds T_{vap}. Since the solids are incompressible, the high temperature and pressure cause the sample to literally explode away from the surface.[47] The amount of material removed per laser shot depends upon a number of factors, including, but not limited to, laser wavelength, pulse width, pulse energy, focal area, and the latent heat of vaporization of the solid matrix.

Samples for laser ablation are most often contained in an air-tight, pressurized cell.[48] The cell has inlet and outlet ports through which argon gas flows. As the sample particles explode away from the surface, they are swept away by the argon stream and into the ICP torch via a connecting tube, where they undergo the subsequent processes of atomization, ionization, etc. Many different versions of these cells have been reported.[40,44,48,49] Of chief importance in the shape and design of the cell is that the flow of argon gas be as laminar as possible for optimum entrainment of the ablated particles. The window must not absorb the incident laser beam; quartz is the typical material.

It is necessary to ablate enough material to achieve and maintain a useful signal level. If the ablated particles are too large, however, they may not be efficiently entrained in the argon stream, and they may deposit within the cell and in the transfer tube.[50] If the laser power is too low, fractional volatilization may occur.[46] And if the rate of particle production is too fast or particle size too large, the plasma may not have sufficient power to completely vaporize them, and the sampler or skimmer cones may clog. Hence, judicious selection of the laser parameters is of paramount importance.

Laser ablation has been to this point, however, a largely semiquantitative technique. This is because of the inherent difficulty of trying to calibrate the signal from the laser ablation of a solid sample of unknown elemental concentration with a “standard” sample. Researchers have attempted to surmount this challenge by a number of methods. One method is to compare the signal from the unknown with the signal obtained from a standard of similar matrix composition.[51] Commercially available standards do exist for solid samples of a variety of matrices, such as metals, coals, glasses, powders, etc.[52] Alternatively, some researchers have attempted to create standards. This is done either by pressing together a "pellet" of matrix and standard materials to resemble the sample, or by grinding the sample together with one or more internal standards, combining together with a suitable binder, and pressing into a pellet.[53] The latter of these two is particularly unattractive, in that it robs laser ablation of some of its primary advantages; i.e. reduced sample preparation and analysis times, possible introduction of contaminants, and loss of spatial information. The overlying difficulty with these is that the standard and the sample must be of virtually the same matrix, the standards must contain the elements of interest in the proper concentration ranges, and the standards and sample must be analyzed separately.

Thesis Objectives and Organization

Because of the relative ease of determining the concentration of liquids with solution standards, it is clear to see how beneficial it would be if solutions could also be used to calibrate the concentration of solid samples. This thesis demonstrates the feasibility of just such an approach.

Chapter 2 is a paper that describes a method for calibrating laser ablation by solution nebulization, and a calibration formula developed in this research group. In this approach, solid particles from an ablation cell are introduced to the plasma simultaneously with desolvated particles from an ultrasonic nebulizer. This method provides fully quantitative analysis of solid samples by laser ablation with excellent agreement with certified standards.

Chapter 3 is a general conclusion with suggestions for future work in the areas presented here, as well as future work with the twin-quadrupole device.

References

1. Houk, R. S., *Acc. Chem. Res.*, 1994, **27**, 333.
2. Hieftje, G. M., and Norman, L. A., *Int. J. Mass Spectrom. Ion Processes*, 1992, **118/119**, 519.
3. Jarvis, K. E., Gray, A. L., and Houk, R. S., *Handbook of Inductively Coupled Plasma Mass Spectrometry*, Blackie & Son, Glasgow, 1992.
4. Houk, R. S., Fassel, V. A., Flesch, D. D., Svec, H. J., Gray, A. L., and Taylor, C. E., *Anal Chem.*, 1980, **52**, 2283.
5. Joannon, S., Telouk, P., and Pin, C., *Spectrochim. Acta, Part B*, 1997, **52**, 1783.
6. Makishima, A., Nakamura, E., and Nakano, T., *Anal. Chem.*, 1997, **69**, 3754.
7. Hall, G. E. M., and Pelchat, J., *J. Anal. Atom. Spectrom.*, 1997, **12**, 103.
8. Crain, J.S., *Spectroscopy*, 1996, **11**, 30.
9. Erickson, M., Aldstadt, J., and Alvarado, J., *J. Haz. Mat.*, 1995, **41**, 351.
10. Heres, A. P., and Noe, M.C., *Nuclear Technology*, 1996, **115**, 146.
11. Liaw, M., Jiang, S., and Li, Y., *Spectrochim. Acta, Part B,* 1997, **52**, 779.
12. van den Broeck, K., Vandecasteele, C., and Geuns, J. M. C., *J. Anal. Atom. Spectrom.*, 1997, **12**, 987.
13. Rodushkin, I., and Ruth, T., *J. Anal. Atom. Spectrom.*, 1997, **12**, 1181.

14. Probst, T. U., Berryman, N. G., Lemmen, P., Lothar, W., Auberger, T., Gabel, D., Carlsson, J., Nóbrega, J., Gélinas, Y., and Krushevska, A., Barnes, R., *J. Anal. Atom. Spectrom.*, 1997, **12**, 1243.
15. Larsson, B., *J. Anal. Atom. Spectrom.,* 1997, **12**, 1115.
16. Bhattacharya, R. N., Wiesner, H., and Berens, T. A., *J. Electrochem. Soc.*, 1997, **144**, 1376.
17. Ajluni, C., *Electronic Design*, 1995, **43**, 38.
18. Morin, M., Kimura, T., and Koyanagi, M., *Solid State Tech.*, 1993, **36**, 45.
19. Fucsko, J., Tan, S., and Balazs, M., *J. Electrochem. Soc.*, 1993, **140**, 1105.
20. Lalchev, M., Ionov, I., and Daskalova, N., *J. Anal. Atom. Spectrom.*, 1997, **12**, 21.
21. Watling, R. J., Lynch, B. F., and Herring, D., *J. Anal. Atom. Spectrom.*, 1997, **12**, 195.
22. Greenfield, S., and Montaser, A., in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, Montaser, A., and Golightly, D. W., eds., 2nd edn., VCH, London, 1992.
23. Allen L. A., Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1996.
24. Niu, H., and Houk, R. S., *Spectrochim. Acta, Part B*, 1996, **51B**, 779.
25. Mahoney, P. P., Ray, S. J., and Hieftje, G. M., *Appl. Spectrosc.*, 1997, **51**, 16A.
26. Myers, D. P., Li, G., Mahoney, P. P., and Hieftje, G. M., *J. Am. Soc. Mass Spectrom.*, 1995, **6**, 400.
27. Myers, D. P., Li, G., Mahoney, P. P., and Hieftje, G. M., *J. Am. Soc. Mass Spectrom.*, 1995, **6**, 411.
28. Myers, D. P., Mahoney, P. P., Li, G., and Hieftje, G. M., *J. Am. Soc. Mass Spectrom.*,, 1995, **6**, 920.

29. Bradshaw, N., Hall, E. F. H., and Sanderson, N.E., *J. Anal. Atom. Spectrom.*, 1989, **4**, 801.
30. Walder, A. J., and Freedman, P. A., *J. Anal. Atom. Spectrom.*, 1992, **7**, 571.
30. Koppenaal, D. W., Barinaga, C. J., and Smith, M. R., *J. Anal. Atom. Spectrom.*, 1994, **9**, 1053.
32. Barinaga, C. J., and Koppenaal, D. W., *Rapid Comm. Mass Spectrom.*, 1994, **8**, 71.
33. Eiden, G. C., Barinaga, C. J., and Koppenaal, D. W., *J. Anal. Atom. Spectrom.*, 1996, **11**, 317.
34. Barinaga, C. J., Eiden, G. C., Alexander, M. L., and Koppenaal, D. W., *Fresenius J. Anal. Chem.*, 1996, **355**, 487.
34. Milgram, K. E., White, F. M., Goodner, K. L., Watson, C. H., Koppenaal, D. W., Barinaga, C. J., Smith, B. H., Winefordner, J. D., Marshall, A. G., Houk, R. S., and Eyler, J. R., *Anal. Chem.*, 1997, **69**, 3714.
35. Dawson, P. H., ed., *Quadrupole Mass Spectrometry and its Applications*, Elsevier Scientific Publishing Co., Amsterdam, 1976.
37. Mermet, J. M., and Ivaldi, J. C., *J. Anal. Atom. Spectrom.*, 1993, **8**, 795.
38. Myers, S. A., and Tracy, D. H., *Spectrochim. Acta, Part B*, 1983, **38**, 1227.
39. Warren, A. R., Allen, L. A., Pang, H., Houk R. S., and Janghorbani, M., *Appl. Spectrosc.*, 1994, **48**, 1360.
40. Allen, L. A., Pang, H, Warren, A. R., and Houk, R. S., *J. Anal. Atom. Spectrom.*, 1995, **10**, 267.

41. Allen, L. A., Leach, J. J., Pang, H., and Houk, R. S., *J. Anal. Atom. Spectrom*, 1997, **12**, 171.

42. Allen, L. A., Leach, J. J., and Houk, R. S., *Anal. Chem.*, 1997, **69**, 2384.

43. Clifford, R. H., Montaser, A., and Dolan, S. P., *Anal. Chem.*, 1990, **62**, 2745.

44. Ramsey, M. H., Coles, B. J., Wilkinson, J. J., and Rankin, A. H., *J. Anal. Atom. Spectrom.*, 1992, **7**, 587.

45. Moenke-Blankenburg, L., in *Lasers in Analytical Atomic Spectroscopy*, Sneddon, J., Thiem, T. L., and Lee, Y., eds, VCH, New York, 1997.

46. Russo, R. E., *Appl. Spectrosc.*, 1995, **49**, 14A.

47. Radziemski, L. J., and Cremers, D. A., eds., *Laser-Induced Plasmas and Applications*, Marcel Dekker, New York, 1989.

48. Arrowsmith, P., and Hughes, S., K., *Appl. Spectrosc.*, 1988, **42**, 1231.

49. Walder, A. J., Abell, I. D., Freedman, P. A., and Platzner, I., *Spectrochim. Acta, Part B*, 1993, **49B**, 397.

50. Arrowsmith, P., and Hughes, S. K., *Appl. Spectrosc.*, 1988, **42**, 1231.

51. Jackson, S. E., Longerich, H. P., Dunning, G. R., Fryer, B. J., *Can. Mineral,* 1992, **30**, 1049.

52. NIST Standard Reference Materials Catalog, 1995-1996.

53. Cromwell, E. F., and Arrowsmith, P., *Anal. Chem.*, 1995, **67**, 131.

CHAPTER 3. GENERAL CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK.

The focus of this dissertation has been the calibration of solid sampling by laser ablation ICP-MS with solution standards. Simultaneous introduction of dried solution aerosols from an ultrasonic nebulizer and particles from an ablation cell into an ICP-MS instrument has shown to be quite effective for the determination of elemental concentration in a solid steel sample. A formula has been derived which when used in conjunction with the aforementioned technique can account for the signal contribution of both sources.

Given the applicability of this technique to the analysis of steel samples, it would seem an appropriate extension of this work to attempt to calibrate materials of other matrices. Because of the high coupling efficiency of laser light with steel, its ablation is relatively "easy" compared to other materials. An interesting experiment would be to attempt the calibration of materials whose ablation is not so straightforward. Two exemplary matrices which have attracted interest for LA analysis include glasses and ceramics.[1] Because of the relatively poor coupling of glasses to visible light, the fundamental beam frequency of a Nd:YAG laser would have to be tripled or quadrupled to yield a beam in the ultraviolet.

Although this instrument has proven able to perform well on samples of moderately high concentrations, its sensitivity is relatively poor. It is believed that a great number of ions strike the center electrode of the beam splitter before they have a chance to be deflected. Plans for a re-designed beam splitter have begun. This splitter will have a recessed center electrode, which should help diverge the beam earlier in the separation process. This should allow for greatly improved sensitivity.

The splitter is also not permanently attached to the chamber; rather it rests on a flat platform. Vibrations of the instrument due to the vacuum pumps eventually shake the splitter out of alignment. Alignment of the splitter requires that the vacuum chamber be vented, a process which is both time-consuming and irreproducible. This may be resolved by solidly affixing the splitter to an externally controlled *xyz* platform. In this manner, alignment of the splitter position and subsequent optimization of ion signal could all be done without breaking vacuum. And with electronic control, this could be performed by the operator while the instrument is in use.

Another alternative to the solid splitter electrodes and the long series of ion lenses necessary to transfer the ions to the quadrupole entrances would be the use of ion guides, specifically hexapoles or octapoles. These devices are similar to quadrupoles in that they utilize electrostatically controlled pairs of rods, but as the name implies, have 6 or 8 rods, respectively. The major advantages in using these devices as ion guides is that they have much larger areas of stability in a-q space than does the quadrupole, and operation in the RF-only mode allows virtually 100% transmission of ions of all masses in an ion beam.[2] The operation of a bent or angled multipole has been proposed by some workers: although only a few known instruments utilize bent multipoles, this author is assured that in theory it should be a valid method for the twin-quadrupole device.[3] This should also provide a considerable improvement in sensitivity.

Polyatomic ion interferences in ICP-MS have been a tremendous source of aggravation for analysts since its inception, the most troublesome of which are MO^+. Another source of polyatomic interferences are those derived from Ar.[4] The most common example in ICP-MS is ArO^+, which overlaps with $^{56}Fe^+$, the predominant iron isotope. Other common argide interferences include $^{40}ArOH^+$, which overlaps with $^{57}Fe^+$, $Ar^{35}Cl^+$ with $^{75}As^+$, and Ar_2^+ with $^{80}Se^+$. And the massive peak at $m/z = 39$ in the ICP-MS spectrum from $^{38}ArH^+$ makes the ability to measure $^{39}K^+$ virtually impossible. Several workers have noted the ability to reduce or even eliminate these interferences using a reduced-power condition known as "cool-plasma".[5-7] It would seem a natural extension to assess the feasibility of performing isotope ratios with this instrument using the cool-plasma condition. Preliminary work has been conducted, but is largely unfinished.

References

1. Baker, S. A., Smith, B. W., and Winefordner, J. D., *Appl. Spectrosc.*, 1998, **52**, 154.
2. Szabo, I., *Int. J. Mass Spectrom. Ion Processes*, 1986, **73**, 197.
3. Ng., C., personal communication (1998).
4. Houk, R. S., *Acc. Chem. Res.*, 1994, **27**, 333.
5. Jiang, S.-J., Houk, R. S., and Stevens, M. A., *Anal. Chem.*, 1988, **60**, 1217.
6. Sakata, K., and Kawabata, K., *Spectrochim. Acta, Part B*, 1994, **49**, 1027.
7. Tanner, S. D., *J. Anal. Atom. Spectrom.*, 1995, **10**, 905.

ACKNOWLEDGEMENTS

It would be virtually impossible to personally thank everyone who has had a hand in getting me to this point. The individuals listed here are but a sampling of the people to whom I owe a tremendous debt of gratitude.

First, I would like to thank the boss, Dr. Sam Houk. His guidance, instruction, and patience have been of immeasurable value to me in my time here. I derive a particular amount of pride having worked for the one who invented this technique. His ability to motivate and demand without saying a word inspires me daily to be a better scientist. Our common interests in history and baseball have made for some lively, entertaining, and educational discussions.

I want to thank Southwestern College for the four years I spent there, especially Drs. Terry Barnett and George Gangwere for their excellent science education. Thanks to Coaches Helmer, Kirkland, and Carr, and especially Coach Hunter for helping me to be a man.

I wish to thank my high school chemistry teacher, Mr. Harold Myers, for inspiring me to pursue science, particularly chemistry, as a career. He brought out the best in me and made me realize I was capable of more than average work.

Of all the people I have worked with here, to Lloyd Allen I owe the most thanks. He has been both my mentor and friend, and to a small extent my idol. He set an example few people could match. He taught me how to perform world-class research with a certain amount of brevity thrown in for sanity's sake.

I have had some other great coworkers here, as well. Special thanks to Steve Johnson, for being a great friend, and for helping me to maintain my sanity these last few months. (And for the Officer Darren affair.) I also want to particularly acknowledge Ma'an Amad, Scott Clemons, Al Gwizdala, Mike Minnich, Sahana Mollah, and Narong Praphairaksit, from each of whom I have learned different lessons beyond just chemistry: life, tolerance, other cultures, and the ability to work with others when I didn't necessarily share their viewpoints. These lessons have been as valuable as any I've gotten here. I've also had the pleasure to work with three undergraduates here; Dave Aeschliman, Sarah Dannen, and Katy Fowler.

This work has been performed at the Ames Laboratory under contract no. W-7405-ENG-82 with the U. S. Department of Energy. The U. S. Government has assigned report number IST-1811 to this thesis.

Thanks to Frank, Keith, Gary, Jenny, Oz, and all the other folks in the storeroom and warehouse, especially Brian. And to all the guys in the machine and glass shops, especially Trond Forre, for all the work they have done for me.

I would like to thank Ho-Ming Pang for all his help with the laser system and the counting software for the twin-quad. And to Dave Eckels for coming to my rescue so many times with the RF generator.

Thanks to Jimi, James, Dave, and The Gear Daddies for late-night inspiration.

To Kim, for being my best friend and supporter.

Thanks to the fellas.

Thanks to my extended family, for being an unfailing source of inspiration and strength whenever I needed it. Special thanks to Randy and Jane and Leon and Rob for being

my surrogate parents in Iowa. And to Uncle Leon for kicking my butt back into shape and not letting me feel sorry for myself when times were tough.

Lastly, but most important of all, I want to thank my immediate family. I would have never made it through this without you. I love you all very much and owe you more than I could ever hope to repay. To my parents, who sacrificed so much to make sure I got a college education - this is your thesis.