IS-T 1798

RECEIVED
JAN 22 1997
OSTI

Inductively coupled plasma mass spectrometry with a twin quadrupole instrument using laser ablation sample introduction and monodisperse dried microparticulate injection

by

Allen, Lloyd A.

PHD Thesis submitted to Iowa State University

Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011

Date Transmitted: October 17, 1996

MASTER

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY

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

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

TABLE OF CONTENTS

Reprint — Removed for separate processing

Preprint — Removed for separate processing

Preprint Removed for separate processing

Fun Typ.

ABSTRACT

The focus of this dissertation is the use of a twin quadrupole inductively coupled plasma mass spectrometer (ICP-MS) for the simultaneous detection of two m/z values.

The twin quadrupole ICP-MS is used with laser ablation sample introduction in both the steady state (10 Hz) and single pulse modes. Steady state signals are highly correlated and the majority of flicker noise cancels when the ratio is calculated. Using a copper sample, the isotope ratio $^{63}Cu^+/^{65}Cu^+$ is measured with a relative standard deviation (RSD) of 0.26%. Transient signals for single laser pulses are also obtained. Copper isotope ratio measurements for several laser pulses are measured with an RSD of 0.85%.

Laser ablation (LA) is used with steel samples to assess the ability of the twin quadrupole ICP-MS to eliminate flicker noise of minor components of steel samples. Isotopic and internal standard ratios are measured in the first part of this work. The isotope ratio $^{52}Cr^+/^{53}Cr^+$ (Cr present at 1.31%) can be measured with an RSD of 0.06% to 0.1%. For internal standard elements, RSDs improve from 1.9% in the Cr^+ signal to 0.12% for the ratio of $^{51}V^+$ to $^{52}Cr^+$. In the second part of this work, one mass spectrometer is scanned while the second channel measures an individual m/z value. When the ratio of these two signals is calculated, the peak shapes in the mass spectrum are improved significantly.

Pulses of analyte and matrix ions from individual drops are measured simultaneously using the twin quadrupole ICP-MS with monodisperse dried microparticulate injection (MDMI). At modest Pb concentrations (500 ppm), a shoulder on the leading edge of the Li^+ signal appears. At higher matrix concentrations (1500 ppm), a dip in the leading edge of the Li^+ signal becomes apparent. Space charge effects are consistent with the disturbances seen. A model for this behavior is proposed. In this model, deflection of Li^+ by space charge causes part of the ion cloud to be driven ahead of the Pb^+ and part to be trapped behind the Pb^+ cloud resulting in a shoulder on the Li^+ signal.

CHAPTER 1. GENERAL INTRODUCTION

Inductively coupled plasma mass spectrometry (ICP-MS) has become a widely used technique for trace elemental and isotopic analysis [1-3]. Attractive features of ICP-MS include detection limits routinely in the part per trillion (pptr) range, a linear dynamic range of 6 to 8 orders of magnitude, and the ability to rapidly, semiquantitatively analyze a single sample for 70 elements while using only a few standard elements[2].

ICP-MS has developed rapidly since its inception in 1980[4]. The attractive features and rapid development have enabled scientists in many disciplines to benefit from the attributes of ICP-MS. These fields include geochemistry[5,6], the semiconductor industry[7,8], environmental chemistry[9,10], clinical chemistry[11,12], and the nuclear industry[13] to name a few.

Problems associated with the early ICP-MS instruments have been identified and, in many cases, ways around these problems have been found. Polyatomic ion interferences originating from the solvent have been attenuated to levels at which practical analysis can be accomplished[14-17]. The dynamic range of ICP-MS has been extended by using new types of detectors[18]. Matrix effects due to space charge in the mass spectrometer have been described[19,20] and new instrumentation has been developed that minimizes the m/z dependence of these matrix effects[21-23]. Space charge is, however still under investigation and new solutions to this problem are being sought out. Finally, sources of noise associated with ICP-MS have been characterized in an effort to improve the precision attainable in ICP-MS[24-27].

In this general introduction, the instrumentation and sample introduction systems used for ICP-MS will be discussed. Attributes and problems of the currently available systems will be illustrated. Sources of noise associated with ICP-MS and the implications of these noise sources to certain types of analyses will be addressed. The combination of instrumentation, sample introduction, and sources of noise associated with ICP-MS lead into the research to which this dissertation is devoted.

ICP-MS Instrumentation

The instrumentation used in all ICP-MS instruments can be broken into three sections; first, the ICP, second, the extraction system and ion optics, and third, the mass analyzer and detector. A schematic diagram of a basic system containing these individual sections is shown in Fig. 1. Each of these basic sections will be discussed in more detail below.

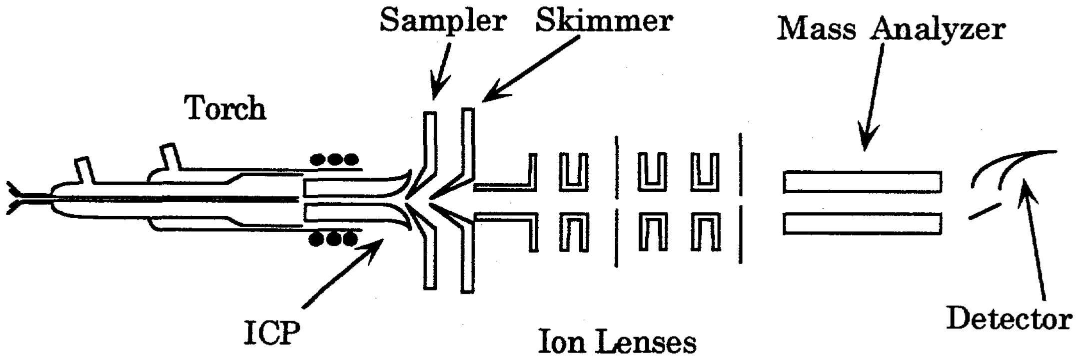

Fig. 1. Schematic diagram of a typical ICP-MS device

The ICP is an electrical discharge sustained in an argon (Ar) atmosphere. Radio frequency (RF) power (typically 700-1500 Watts) is supplied to a coil, known as the load coil, that surrounds a quartz torch. The torch consists of several concentric tubes to which different flows of Ar are supplied. The largest amount of Ar (~ 16 l min^{-1}) is introduced to the outermost region of the torch and is commonly referred to as the outer gas. RF power supplied to the load coil directly interacts with the outer gas to form a zone known as the induction region. A second flow of Ar is added to the middle concentric tube of the torch. This flow, commonly known as the auxiliary or make-up flow, is typically about 1 l min^{-1} although a large range of flows are used. The third Ar flow to the torch is used to transport the sample from the sample introduction system (see next section) to the plasma. Usually called the nebulizer flow, this flow "punches" a hole through the plasma to form a relatively cool region referred to as the central channel. In this fashion, power applied from the load coil does not directly interact with the sample, rather it is indirectly coupled to the sample through the induction region. A typical flow rate used for the nebulizer flow is 1 l min^{-1}.

In the plasma, the sample is dissociated, atomized and ionized. For the most part, singly charged atomic ions are formed which are extracted into the mass analyzer.

The extraction system used in most ICP-MS instruments consists of a sampler and skimmer[27]. Ions created in the plasma must be transported from the ICP to a vacuum system capable of maintaining pressures suitable for analysis by mass spectrometry ($\sim 10^{-5}$ torr). The plasma, as a quasineutral mixture of neutral atoms, electrons, and ions, is first extracted through the sampler cone (typical orifice diam. = 1 mm) and into the first vacuum stage where the pressure is typically about one torr. A supersonic jet is formed from the extracted plasma in the first stage. In the axial direction, the supersonic jet is free from collisions to a zone known as the Mach disc. At the onset of the Mach disc, the extracted plasma and background gases collide. A second cone, known as the skimmer (typical orifice diam. = 1 mm), is inserted through the Mach disc into the supersonic jet expansion (also known as the zone of silence). The pressure in the region behind the skimmer is typically $\sim 10^{-4}$ torr. As the mixture of neutral atoms, ions and electrons expands behind the skimmer, interactions with the first ion lens begin to occur. The quasineutral state breaks down and a beam comprised mainly of singly charged positive ions is formed. A detailed description of the extraction process is given elsewhere[29].

The extracted ion beam is transferred through a set of ion lenses into the third pumping stage of the system where the pressures are typically 5×10^{-5} torr or less during operation. The beam is then guided through more ion lenses to the mass analyzer.

Several types of mass analyzers have been used in conjunction with the ICP including quadrupole[1-17,19-23], double focusing magnetic sector[29,30], ion trap[31,32], and time of flight[33,34]. Each of these mass analyzers is unique in the technique used to differentiate ions of different m/z values. A detailed description of each type of mass analyzer is beyond the scope of this discussion. Suffice to say, each mass analyzer has advantages and drawbacks.

Due to the robustness and ease of operation, the quadrupole is by far most common type of mass analyzer used in conjunction with the ICP. Popular though it may be, the quadrupole does have limitations. Since only one m/z value is transmitted at a time, the majority of ions transmitted to the quadrupole are discarded. Also, in order to do multielement (i.e. multi m/z) determinations, the quadrupole must be rapidly peak hopped or scanned. Peak hopping or scanning can limit the precision obtained when doing isotope ratio measurements (see Sources of Noise).

The type of device used for detection of the mass resolved ion varies depending on the type of mass analyzer used. For a typical quadrupole system, electron multipliers are most commonly employed. Basically, the mass resolved ion impacts the detector which begins an electron avalanche. From this electron avalanche, an analog signal is produced which can be processed in different ways to yield a readable signal.

Sample Introduction Techniques

Samples are usually delivered to the ICP as a fine mist of aqueous droplets known as an aerosol. The device which generates the aerosol is generally termed a nebulizer. There are several different ways in which an aerosol can be generated. In the most common type of nebulizer, known as a pneumatic nebulizer, aqueous sample is delivered to a thin quartz tube which is surrounded by a larger concentric tube. Argon gas flows through the outer tube and as the sample is delivered to the tip of the inner tube, the gas shatters the liquid into a polydisperse aerosol. The largest droplets are removed from the aerosol by a spray chamber and only the smallest droplets are introduced to the plasma. As such, only about 2% of the nebulized sample actually enters the plasma. The droplets that are transported to the plasma are polydisperse in nature and are thought to be a major cause of flicker noise in the plasma[36-38].

Several different types of nebulizers have been introduced in recent years with the advantage of increased efficiency. These include the ultrasonic nebulizer[39,40], direct injection nebulizer[41-43], the hydraulic high pressure nebulizer[44,45] and the monodisperse dried microparticulate injector (MDMI)[46]. The increased efficiency of these nebulizers has enabled increased sensitivity and lower sample consumption in ICP-MS.

Advantages of solution sample introduction include relative ease of calibration and possibility of chromatographic separation prior to introduction. In cases where the original sample is a solid, solution sample introduction does, however, have drawbacks. These drawbacks include time consuming dissolution procedures, the possibility of contaminating the sample during dissolution, and occurrence of interferences in the mass spectrum arising from polyatomic ions derived from the solvent.

Solid sample introduction has also been used in conjunction with ICP-MS. Several systems have been used for solid sample introduction including laser ablation (LA)[47-49], arc nebulization[50,51], direct sample insertion[52,53], and electrothermal vaporization[54,55]. Advantages of solid sample introduction include no sample dissolution and lack of solvent related spectral interferences. However, due to the lack of matrix matched standard materials, calibration is complicated and quantitative analysis is difficult.

Sources of Noise in ICP-MS

The precision attainable for any analytical method is based on the reproducibility of the technique. ICP-MS can obtain a precision level for an individual signal of about 2-3% relative standard deviation (RSD) and about 1% RSD when an internal standard is used.

Several sources of noise contribute to the total noise level seen in ICP-MS. Two of these are flicker noise and shot noise. Flicker noise is a non-fundamental noise source arising mainly from the plasma and sample introduction system. The flicker noise contribution to the overall noise level increases directly with the signal. Shot noise is a fundamental source of noise due to the random arrival of particles (ions in case of ICP-MS) at a detector. The level of shot noise on a signal is proportional to the square root of the signal.

At high signal levels, flicker noise is typically the dominant source of noise in ICP-MS measurements. High precision measurement of isotope ratios ($\mathrm{RSD} \leq 0.1\%$) is difficult in quadrupole ICP-MS. To minimize the effects of flicker noise, the quadrupole must be rapidly peak hopped to the isotopes of interest. During rapid peak hopping, the amount of signal acquired is small and precision can become limited by shot noise. This problem is worse for noisy steady state sample introduction systems such as LA and systems which yield transient signals such as chromatography, flow injection, and single shot LA. For these reasons, ICP-MS has not seen widespread use for high precision isotope ratio measurements.

High precision isotope ratio measurements are important in the nuclear industry[13], geochemistry[56,57] and clinical chemistry[58]. Currently, thermal ionization mass spectrometry (TIMS) dominates the field of high precision isotope ratio measurement[56,59]. However, the time consuming sample preparation and data acquisition as well as isotope fractionation make TIMS less than ideal. Clearly, a quadrupole ICP-MS system capable of high precision isotope ratio measurements would be a welcome addition to the field of high precision isotope ratio measurements.

Dissertation Objectives and Organization

Using ICP emission spectroscopy, several groups have shown that simultaneous detection of different lines is an effective method of removing flicker noise[60,61]. In ICP-MS, Walder *et al.*[62-64] developed a double focusing magnetic sector mass analyzer equipped with multiple Faraday cup collectors for simultaneous detection of up to 9 adjacent m/z values. Using this instrument, isotope ratios with a precision that approaches that of TIMS have been obtained. However, the multicollector ICP-MS device is large and expensive. Since the position of each detector is fixed, the device is not capable of scanning. As such, the multicollector has, to this point, only been used for isotopic analysis.

The emphasis of this thesis is the use of a unique, quadrupole based ICP-MS instrument that enables simultaneous detection of two m/z values. This device, known as the twin quadrupole ICP-MS[65], was suggested by M. Janghorbani and designed largely by A. R. Warren. The extracted ion beam is split into two parts. Each part is then sent to its own quadrupole mass analyzer and detector. In this work, the twin quadrupole ICP-MS is used in conjunction with solid sample introduction by LA and solution sample introduction using the MDMI.

Chapters 2, 3, and 4 of this thesis each stand alone as individual scientific manuscripts and are either published, submitted for publication or ready for submission to a scientific journal. Chapter 5 is a general conclusion with suggestions for future research in the areas presented in the previous chapters.

Chapter 2 presents isotope ratio measurements using LA sample introduction of a copper sample. Copper isotope ratios are measured for both steady state (10 Hz laser repetition rate) and transient signals resulting from a single laser pulse. In this chapter, the sensitivity of the instrument is mediocre, however cancellation of flicker noise in both the steady state and transient case is demonstrated. The measured precision of the isotope ratio is poorer than the theoretical counting statistics limit, however a significant improvement in precision is realized when using simultaneous detection.

Improvements were made to the instrument resulting in higher sensitivity and improved precision. These results are discussed in Chapter 3 using LA sample introduction of steel standard reference materials. Isotope ratio measurements are made with a precision that is shown to be limited by counting statistics. Isotopes of two different elements (i.e. internal standards) are also measured. The precision of the ratio of isotopes of two different elements is poorer than the precision of isotopes of the same element. Significant reduction in flicker noise is, however, demonstrated for a wide range of internal standard elements. Chapter 3 also presents results in which one quadrupole is scanned while the other quadrupole remains in the single ion monitoring mode. When the ratio of these two signals is taken, spikes in the mass spectrum resulting from flicker noise in the plasma and sample introduction system cancel and a smoother mass spectrum results.

In chapter 4, the MDMI is used to introduce individual droplets to the plasma. Ion signals from individual droplets are measured simultaneously. The effect of a high concentration of heavy, easily ionized matrix ion (Pb) on a light, easily ionized analyte (Li) is evaluated. As the concentration of Pb is increased, a shoulder on the leading edge of the $^{7}Li^{+}$ signal is seen. Deflection of ions due to space charge in the extraction system and ion optics of the mass spectrometer are consistent with the observed signals. An intuitive depiction for this behavior is presented. This depiction indicates that the first extraction lens may have an effect on the profile seen. The voltage applied to the extraction lens is increased and a change in the profile is observed.

References

1. Houk, R. S., *Acc. Chem. Res.*, 1994, **27**, 333.
2. Jarvis, K. E., Gray, A. L., and Houk, R. S., *Handbook of Inductively Coupled Plasma Mass Spectrometry*, Blackie & Son, Glasgow, 1992.
3. Hieftje, G. M., and Norman, L. A., *Int. J. Mass Spectrom. Ion Processes*, 1992, **118/119**, 519.
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. Jarvis, K. E., *Chem. Geol.*, 1988, **68**, 31.
6. Feng, R., Machado, N., Ludden, J., *Geochim. Cosmochim. Acta*, 1993, **57**, 3479.
7. Tan, S. H., *Nucl. Inst. and Meth. in Phys. Res. B*, 1995, **99**, 458.
8. Fucsko, J., Tan, S. H., and Balazs, M. K., *J. Electrochem. Soc.*, 1993, **140**, 1105.
9. Dolan, R., Van Loon, J., Templeton, D., and Paudyn, A., *Fresenius' J. Anal. Chem.*, 1990, **336**, 99.
10. Takunori, K., Nakamura, S., and Morita, M., *Anal. Sci.*, 1990, **6**, 623.
11. Mulligan, K. J., Davidson, T. M., and Caruso, J. A., *J. Anal. At. Spectrom.*, 1990, **5**, 301.
12. Ting, B. T. G., and Janghorbani, M., *Spectrochim. Acta, Part B*, 1987, **42**, 21.

13. *Applications of Inductively Coupled Plasma Mass Spectrometry to Radionuclide Determinations*, eds. Morrow, R. W., and Crain, J. S., American Society of Testing and Materials, Philadelphia, P. A., 1995.

14. Alves, L. C., Wiederin, D. R., and Houk, R. S., *Anal. Chem.*, 1992, **64**, 1164.14.

15. Alves, L. C., Allen, L. A., and Houk, R. S., *Anal. Chem.*, 1993, **65**, 2468.

16. Alves, L. C., Minnich, M. G., Weiderin, D. R., and Houk, R. S., *J. Anal. At. Spectrom.*, 1994, **9**, 399.

17. Tao, H., and Miyazaki, A., *J. Anal. At. Spectrom.*, 1995, **10**, 1.

18. Stresau, D., and Hunter, K., poster presented at the 41st ASMS Conference on Mass Spectrometry and Allied Topics, San Fransisco, CA, May 31 to June 4, 1993.

19. Gillson, G. R., Douglas, D. J., Fulford, J. E., Halligan, K. W., and Tanner, S. D., *Anal. Chem.*, 1988, **60**, 1472.

20. Tanner, S. D., *Spectrochim. Acta, Part B*, 1992, **47**, 809.

21. Turner, P., In *Applications of Plasma Source Mass Spectrometry*, Holland, G., Eaton, A. N., Eds; Royal Society of Chemistry, Cambridge, 1993.

22. Tanner, S. D., Douglas, D. J., and French, J. B., *Appl. Spectrosc.* 1994, **48**, 1367.

23. Tanner, S. D., Cousins. L. M., and Douglas, D. J., *Appl. Spectrosc.*,1994, **48**, 1367.

24. Luan, S., Pang, H., Shum, S. C. K., and Houk, R. S., *J. Anal. At. Spectrom.*, 1992, **7**, 799.

25. Ince, A. T., Williams, J. G., and Gray, A. L., *J. Anal. At. Spectrom.*, 1993, **8**, 899.

26. Gray, A. L., Williams, J. G., Ince, A. T., and Liezers, M., *J. Anal. At. Spectrom.*, 1995, **10**, 569.

27. Begley, I. S., and Sharp, B. L., *J. Anal. At. Spectrom.*, 1994, **9**, 171.

28. Olivarez, J., and Houk, R. S., *Anal. Chem.*, 1985, **57**, 2674.

29. Niu, H., and Houk, R. S., *Spectrochim. Acta, Part B*, 1996, **51**, 779.

30. Moens, L., Vanhaecke, F., Riondato, J., and Dams, R., *J. Anal, At. Spectrom.*, 1995, **10**, 569.

31. Vanhaecke, F., Moens, L., Dams, R., and Taylor, P., *Anal. Chem.*, 1996, **68**, 567.

32. Barinaga, C. J., and Koppenaal, D. W., *Rapid Commun. Mass Spectrom.*, 1994, **8**, 71.

33. Koppenaal, D. W., Barinaga, C. J., and Smith, M. R., *J. Anal. At. Spectrom.*, 1994, **9**, 1053.

34. Myers, D. P., Li, G., Mahoney, P. P., and Hieftje, G. M., *J. Am. Soc. Mass Spectrom.*, 1995, **6**, 400.

35. Myers, D. P., Li, G., Mahoney, P. P., and Hieftje, G. M., *J. Am. Soc. Mass Spectrom.*, 1995, **6**, 411.

36. Winge, R. K., Crain, J. S., and Houk, R. S., *J. Anal. At. Spectrom.*, 1991, **6**, 601.

37. Hobbs, S. S., and Olesik, J. W., *Anal. Chem.*, 1992, **64**, 274.

38. Olesik, J. W., and Fister, J. C., *Spectrochim. Acta, Part B*, 1991, **46**, 851.

39. Thompson, J. J., and Houk, R. S., *Anal. Chem.*, 1986, **58**, 2541.

40. Montaser, A., Tan, H., Ishii, I., Nam, S.-H., and Cai, M., *Anal. Chem.*, 1991, 63, 2660.

41. Wiederin, D. R., Smith, F. G., and Houk, R. S., *Anal. Chem.*, 1991, **63**, 219.

42. Wiederin, D. R., Smyczek, R. E., and Houk, R. S., *Anal. Chem.*, 1991, **63**, 1626.

43. Shum, S. C. K., Johnson, S. K., Pang, H., and Houk, R. S., *Appl. Spectrosc.*, 1993, **47**, 575.

44. Jakubowski, N., Feldmann, I., Stuewer, D., and Berndt, H., *Spectrochim. Acta, Part B*, 1992, **47**, 119.

45. Jakubowski, N., Jepkens, B., Stuewer, D., and Berndt, H., *J. Anal. At. Spectrom.*, 1994, **9**, 193.

46. French, J. B., Etkin, B., and Jong, R., *Anal. Chem.*, 1994, **66**, 685.

47. Gray, A. L., *Analyst*, 1985, **110**, 551.

48. Kogan, V. V., Hinds, M. W., and Ramendik, G. I., *Spetrochim. Acta, Part B*, 1994, **49**, 205.

49. Chenery, S., and Cook, J. M., *J. Anal. At. Spectrom.*, 1993, **8**, 299.

50. Jiang, S.-J., and Houk, R. S., *Anal. Chem.*,1986, **58**, 1736.

51. Jiang, S.-J., and Houk, R. S., *Spectrochim. Acta, Part B*, 1987, **42**, 9312.

52. Bloomer, D. W., Powell, M., Sing, R. L. A., and Salin, E. D., *Anal. Chem.*, 1986, **58**, 975.

53. Karanassios, V., and Horlick, G., *Spectrochim. Acta Rev.*, 1990, **13**, 89.

54. Park, C. J., Hall, G. E. M., *J. Anal. At. Spectrom.*, 1987, **2**, 473.

55. Völlkopf, U., Paul, M., and Denoyer, E. R., *Fresenius' J. Anal. Chem.*, 1992, **342**, 1421.

56. Faure, G., *Principles of Isotope Geology*, chapt. 5, Wiley, New York, 1986.

57. Fryer, B. J., Jackson, S. E., and Longerich, H. P., *Chem. Geol.*, 1993, **109**, 1.

58. Delves, H. T., and Campbell, M. J., *J. Anal. At. Spectrom.*, 1988, **3**, 343.

59. Yaffe, Y., Flessel, C. P., del Rosano, A., Matias, V., Degarmo, T. E., Coleman, G. C., Gramlich, J., and Kelly, W. R., *Arch. Environ. Health*, 1983, **38**, 237.

60. Mermet, J. M., and Ivaldi, J. C., *J. Anal. At. Spectrom.*,1993, **8**, 795.

61. Myers, S. A., and Tracy, D. H., *Spectrochim. Acta, Part B*, 1983, **38**, 1227.

62. Walder, A. J., Abel, I. D., Platzner, I., and Freedman, P. A., *Spectrochim. Acta, Part B*, 1993, **48**, 397.

63. Walder, A. J., Platzner, I., and Freedman, P. A., *J. Anal. At. Spectrom.*, 1992, **7**, 571.

64. Walder, A. J., Platzner, I., and Freedman, P. A., *J. Anal. At. Spectrom.*, 1993, **8**, 19.

65. Warren, A. R., Allen, L. A., Pang, H., Houk, R. S., and Janghorbani, M., *Appl. Spectrosc.*, 1994, **48**, 1360.

CHAPTER 5. GENERAL CONCLUSION

The focus of this dissertation has been the use of the twin quadrupole ICP-MS device in conjunction with LA and MDMI. The aim has been the removal of flicker noise from the plasma and sample introduction system and fundamental study of matrix effects due to space charge in the mass spectrometer.

Chapter 2 demonstrated the ability of the twin quadrupole to effectively eliminate flicker noise during steady state and transient (single laser pulse) sample introduction using LA. The ability to do isotope ratio measurements using single laser shots could become an important tool in geochemistry where elemental and isotopic analysis of single mineral grains has already been done[1].

Chapter 3 reported on improvements in sensitivity and precision of the twin quadrupole ICP-MS. LA was used to introduce steel reference materials. Isotope ratio measurements were found to be limited by counting statistics for dwell times of 2 sec. and less. An internal standard was used to compensate for flicker noise during multielement determinations. The simultaneous detection capability of the twin quadrupole device make this correction very good, however, this procedure could also be used with commercial ICP-MS instruments to compensate for flicker noise during multielement determinations.

In chapter 4, the MDMI was used to introduce individual particles to the ICP. Fast data acquisition was used and it was shown that the onset of and the maximum ion signal in each channel of the device are correlated in time. $^{7}Li^{+}$ ion signals were measured with and without a matrix concentration of Pb. As the concentration of Pb was increased, first a shoulder and then a dip was noticed on the leading edge of the $^7Li^+$ signal. Using the twin quadrupole device, $^7Li^+$ and $^{206}Pb^+$ ion signals produced from a single drop were detected simultaneously. Simultaneous detection gave additional information on the interaction of a heavy matrix ion with a light analyte ion. The observed effects are most likely due to space charge repulsion in the extraction system and ion optics of the mass spectrometer.

To date, the work that has been done using the twin quadrupole ICP-MS has demonstrated the usefulness of a quadrupole based system that give simultaneous detection. However, in order for this device to become established in the analytical community several problems need to be addressed.

First, although improved from earlier experiments, the sensitivity of the instrument must be increased. One possible way this might be realized is by using a different type of splitting device. The current splitting device is rigid and alignment of the splitter with both quadrupoles is difficult. A compromise position for both quadrupole entrances has been used up to this point. Independent alignment of both sides of the splitter could be accomplished using a metal mesh material. A splitter made from mesh could extend from the initial splitting point to the entrance of the quadrupoles with only a small separation allowed for ion optics.

Second, a recurring problem has been the inability to further improve the precision of a ratio measurement by extending the dwell time past 2 sec. Although it is still unclear why further extension of dwell time is not beneficial, one possibility is detector instability. To this point, channeltron electron multipliers (CEM) have been used for ion detection. Most commercial ICP-MS instruments now use discrete dynode detectors. The use of these type of detectors may be helpful in extending dwell times and accumulation of more signal to further improve the precision of ratio measurements.

Finally, when using the MDMI in the horizontal orientation, reproducible transport of droplets/particles to the plasma is difficult. A possible way around this problem is to construct a vertical ICP-MS device. This idea has, in fact, been proposed by others[2], and conversion of the twin quadrupole ICP-MS to the vertical orientation should prove helpful when using the MDMI.

References

1. Chenery, S., and Cook, J. M., *J. Anal. At. Spectrom.*, 1993, **8**, 299.
2. Olesik, J. W., and Dziewatkoski, M. P., *J. Am. Soc. Mass Spectrom.*, 1996, 7, 362.

ACKNOWLEDGEMENTS

It is difficult for me to give adequate thanks each person who has helped me through me educational experience. The individuals named here are but a few of those who have had a direct impact on the work that has gone into my education, and my thesis work in particular.

First, I would like to thank my major professor, Dr. R. S. Houk. His guidance and instruction during the course of my graduate studies have truly opened my eyes to the joys of research. I feel very fortunate to have been able to work for Dr. Houk and know that the education I have received at Iowa State is exceptional.

I wish to thank the individuals with whom I have worked. In particular, Luis Alves, Arnold "Rocky" Warren, Ho-Ming Pang, James "Jay" Leach, Sara Dannon, and David Aeschilman. I thank Luis for giving me my first glance at research in analytical chemistry. I thank Rocky for allowing me to work with him on the initial twin quadrupole experiments. The early days were challenging, frustrating, and exciting. I thank Ho-Ming for his insight on a number of projects. He was a great resource throughout my graduate career. I thank Jay for the help he has given me on the work in the latter portion of this thesis. I have had the opportunity to work with two undergraduate students in the final months at Iowa State, Sara and Dave. I thank you all for your assistance and wish you well as you continue your education.

This work was performed at Ames Laboratory under Contract No. W-7405-Eng-82 with the U.S. Department of Energy. The United States government has assigned the DOE

Report number IS-T 1798 to this thesis.

I would like to thank David Eckles for his assistance in bringing back to life (several times) the RF generator used in this work. His knowledge and persistence were a great help.

I would like to thank all the current and former Houk group members with whom it has been a pleasure to work: Ke Hu, Sam Shum, Hongsen Niu, Xiaoshan Chen, P. Scott Clemons, Shen Luan, Renyi Duan, Steve Johnson, Tonya Bricker, Mike Minnich, Albin "Al" Gwizdala III, Narong Praphairaksit, Maan Amad, Elise Luang, Jin Wang, Sahanna Mollah and Zhiyang Du. I wish each and every one of you the best and hope to keep in contact with you in the years to come.

I would like to thank the University of Wisconsin-LaCrosse for an excellent undergraduate education. In particular, I wish to thank Dr. Paul Taylor for his guidance as I chose a career in analytical chemistry.

I wish to thank my entire family. I thank my parents for the support they provided and the example they set which have been a source of comfort and inspiration throughout my education. I thank my brother, Martin, and his wife, Melissa, for all their help and support. I thank the rest of my family for their encouragement which has been infinitely helpful during my studies.

Most of all, I wish to thank my wife, Michelle. Her love, support, understanding, and encouragement have been the ultimate blessing during graduate school. The dedication that she shows to her craft has been a source of inspiration. I feel very fortunate to have been able to share my time in graduate school with her.