IS-T 1802

Unique applications of solvent removal in inductively coupled plasma mass spectrometry

by

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MS Thesis submitted to Iowa State University

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Date Transmitted: January 10, 1997

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. W-7405-Eng-82.

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TABLE OF CONTENTS

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CHAPTER 1. GENERAL INTRODUCTION

Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is the technique of choice for rapid, high precision, semiquantitative elemental and isotopic analysis for over 70 elements.[1-5] Less than 20 years after the first mass spectrum was obtained by ICP-MS,[6] this technique has applications in clinical chemistry,[7,8] geochemistry,[9-15] the semiconductor industry,[16,17] the nuclear industry,[18-20] environmental chemistry,[11,18,21-26] and forensic chemistry.[27]

Through advances in instrumentation, detection limits are routinely achievable to part per trillion levels and, on some commercial instruments, even to part per quadrillion levels. The determination of many elements, though, by ICP-MS is complicated by spectral interferences from background species, interelement spectral overlaps, and polyatomic ions of matrix elements.[28-31] A spectral interference occurs when the nominal mass of two species (elemental or polyatomic) is the same. Although there are discrete differences in these masses, the quadrupole instruments generally used do not operate at high enough resolution to distinguish these species.

Background species in ICP-MS are those originating from argon, air, and the nebulized solvent.[30] In aqueous samples, usually acidified with 1% nitric acid, $^{40}Ar^{16}O^+$ interferes with $^{56}Fe^+$, the major isotope of iron. In organic solvents, the determination of Cr^+ at m/z = 52, the most abundant isotope of chromium, is complicated by $^{40}Ar^{12}C^+$.

Some elements have isotopes which overlap with the isotopes of other elements.[31]

Relative abundances of naturally occurring isotopes, which have been tabulated, are used to correct for these interferences. Cadmium, a carcinogen, has eight isotopes at m/z = 106, 108, 110, 111, 112, 113, 114 (major), and 116. However, palladium also has isotopes at m/z = 106, 108, and 110; tin has isotopes at m/z = 112, 114, and 116; and indium has a minor isotope at m/z = 113. Thus, Cd has only one isotope at m/z = 111 (12.7% abundant) completely free of interference from other elements. To determine the presence of these potential interferences, $^{105}Pd^+$, $^{115}In^+$, and $^{118}Sn^+$, which have no other elemental overlaps, must be monitored. In aqueous solution, most elements form oxides and hydroxides which further complicate elemental analysis.[29,32-40] In this example, oxides of molybdenum at m/z = 108, 110, 111, 112, 113, 114, and 116 interfere with all Cd^+ isotopes except m/z = 106 (1.2% abundant). Therefore, the presence of Mo^+ would need to be determined following the guidelines set earlier in this argument.

The sample matrix further complicates the background spectrum.[30] Elemental impurities in the solvent or acid used to prepare the samples combine with the previously mentioned background ions.[28,29] The five isotopes of titanium, a possible impurity in nitric acid, at m/z = 46, 47, 48, 49, and 50 form oxides which overlap with $^{62}Ni^+$, $^{63}Cu^+$, $^{64}Zn^+$, $^{65}Cu^+$, and $^{66}Zn^+$. For this reason, ultrahigh purity reagents and cleanrooms are becoming essential. In some cases, interferences are not preventable. If the sample contains a high chloride content, the determination of vanadium (m/z = 51, 99.7% abundant) and arsenic (m/z = 75, 100% abundant) are complicated by $^{35}Cl^{16}O^+$ and $^{40}Ar^{35}Cl^+$ interferences, respectively.

As analyses approach being limited by the blank, the demands on sample

preparation become more stringent. Although not a requirement for ICP-MS, solutions are beneficial in that they are highly homogeneous, calibration standards are easy to prepare, and blanks can be analyzed. Preparation of solutions, however, is time consuming for ceramics, refractory metals, and metal oxides and also destroys spatial information. Sample preparation may also introduce, either avoidably or unavoidably, impurities which produce interferences. Spectral interferences from the solvent, however, always remain.

Although adjusting operating conditions, such as aerosol gas flow rate, reduce the apparent abundance of metal oxides, there is a compromise in the analyte sensitivity. Generally, it is better to remove interferences than to correct for them especially for determinations at trace levels. Desolvation using an ice water cooled condenser was used in the first ICP-MS device.[6] Cooling the aerosol by this method is sufficient to this day, but there was the potential to remove more solvent by cooling the aerosol to even lower temperatures.

Sample Nebulization and Desolvation

Sample is delivered via peristaltic pump to an ultrasonic nebulizer where the aerosol is generated. The aerosol is created by wetting the surface of a piezoelectric transducer--a quartz crystal to which a radio frequency is applied. As the piezoelectric oscillates, the liquid layer is disturbed and a dense mist of droplets is produced. The aerosol is heated to 40°C above the boiling point of the solvent and cooled to 0°C. This removes most of the solvent and is sufficient in most cases to continue on to the ICP. The process of removing solvent from the aerosol is called desolvation.

Membrane desolvation, a commercially available device, includes a heated microporous Teflon (PTFE) membrane after the ice water condenser. As the aerosol passes the membrane, solvent is vaporized and passes through the membrane. The volatilized solvent is purged by a continuous flow of argon. The dry aerosol then proceeds on to the ICP.

Cryogenic desolvation, a laboratory design, uses a second condenser at -80°C and a series of heating and cooling coils. Solvent enters tangentially through a sidearm in the glass condenser which is immersed in an ethanol bath at -80°C. The aerosol flows downward contacting the walls of the condenser. Solvent vapor freezes along the walls of the condenser and the surviving aerosol makes a second pass through an inner tube before entering a series of copper loops half immersed in the ethanol bath, half heated to 40°C above the boiling point of the solvent. By repeatedly vaporizing the solvent and recondensing it (presumably away from the aerosol particle), a dry aerosol is obtained for transport to the plasma.

The type of nebulizer used is not necessarily important; the focus is on the desolvation method. An ultrasonic nebulizer, as opposed to a pneumatic nebulizer, was used simply to benefit from the increase in sensitivity inherent in the greater total production rate of droplets by the ultrasonic nebulizer.

Previous work by this group describes fundamental studies using cryogenic desolvation.[41-44] Another group has reported results using a similar cryogenic system.[45] More recently, membrane desolvation methods have been investigated.[46]

Thesis Objectives and Organization

The emphasis of this thesis is the unique applications of solvent removal using cryogenic and membrane desolvation. Chapter 1 is a general introduction providing background information concerning the need for these methods and some information about the methods themselves. Chapters 2, 3, and 4 are being prepared as journal manuscripts. Chapter 5 discusses general conclusions and general observations pertaining to this work.

Chapter 2 describes a method to screen urine samples for vanadium at the 12 ppb level using cryogenic desolvation, which attenuates $^{35}Cl^{16}O^+$ to levels low enough that $^{51}V^+$ can be determined. By adding a scandium internal standard to the urine samples, the V^+/Sc^+ signal ratio from each urine sample can be compared to the V^+/Sc^+ signal ratio from a standard solution containing equal concentrations of V^+ and Sc^+. Urine samples can be quickly screened above or below the desired screening concentration determined by the standard ratio solution. Using the signal ratio corrects for signal suppression for different concentrations of matrix elements, like sodium, as well as drift. Quantitative results can also be obtained from the data. Cryogenic desolvation also attenuates $ArCl^+$ facilitating the determination of arsenic and selenium.

Chapter 3 is a comparison of the analytical results obtained by the laboratory-designed cryogenic desolvation system and the commercially available membrane desolvation system. Comparisons are made for sensitivity, oxide ratios, and the difference in aerosol gas flow rate needed to maximize M^+ and MO^+ signals. Of interest to the nuclear industry is the determination of actinide elements which not only form

strong oxides, but also form relatively strong hydrides and hydroxides. Thorium is used to determine whether desolvation can reduce the abundance of these species and, if so, to what extent. Results obtained by determining the vanadium concentration in nasal wash samples using the method from Chapter 2 are compared using cryogenic and membrane desolvation. This manuscript is prepared for submission to a journal to be determined.

Chapter 4 describes a method to suppress Ar^+ and its polyatomics by shielding the plasma from the load coil and adjusting the operating conditions. By positioning a slotted, conductive metal cylinder between the torch and the load coil, the plasma potential is reduced. As a result, the secondary discharge, where troublesome polyatomics are believed to form, is also reduced. The plasma gas flow rate is increased slightly to have a cooling effect on the plasma. This method is used to determine potassium in the presence of 100-fold excess sodium. Although $^{38}ArH^+$ and $^{40}ArH^+$ are suppressed sufficiently to allow measurement of the two most abundant isotopes of K^+ at m/z = 39 and 41, the presence of Na^+ in the sample produces an intense spectral interference at m/z = 41, presumably by $^{23}Na(H_2O)^+$. Since conventional desolvation with an ultrasonic nebulizer did not attenuate this species, the samples were prepared in D_2O so that the sodium-solvent complex would be at m/z = 43, and m/z = 41 would be free. This manuscript is prepared for submission to a journal to be determined.

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Acquisition of a commercially available membrane desolvator, which vaporizes the solvent allowing it to pass through the membrane to vent, permitted comparison with the laboratory-design cryogenic system. The membrane desolvator serves as an "industry standard" to which the performance of cryogenic desolvation can be related. MO^+/M^+, MOH^+/M^+, and MH^+/M^+ are slightly lower for cryogenic desolvation than those for membrane desolvation. A general observation is that cryogenic desolvation may remove nitric acid to a greater extent than membrane desolvation. Compared to conventional desolvation with an ultrasonic nebulizer, membrane desolvation moves the M^+ and MO^+ peak maxima farther apart while cryogenic desolvation moves the two peak maxima closer together. Since oxide ratios are at least the same order of magnitude, cryogenic desolvation must narrow the profile of species count rate as a function of aerosol gas flow rate. Cryogenic and membrane desolvation can be operated alternately without extinguishing the plasma and with little re-optimization. Results obtained by the two methods for identical samples agree within 5%.

For some elements, adjusting the plasma operating conditions and mechanically reducing the secondary discharge to achieve a cool plasma condition is necessary. The cool plasma mass spectrum is very different from the normal plasma spectrum. For the determination of potassium, the cool plasma frees m/z = 41 of $^{40}ArH^+$. However, the presence of sodium in the sample produces $^{23}Na(H_2O)^+$ at the same mass. Since conventional desolvation with an ultrasonic nebulizer could not attenuate this species, the solvent was used to advantage. By preparing the samples in D_2O, the Na^+ would form a complex at m/z = 43 freeing m/z =41 for determination of potassium by isotope

dilution.

In the recent past, cryogenic desolvation was criticized for losing sensitivity compared to the nebulizer alone. This is true, if operating at the same aerosol gas flow rate for both methods. If the aerosol gas flow rate is optimized for each method, the maximum sensitivities achievable are approximately the same. Removing solvent changes conditions in the plasma so there is a need for re-optimization.

Previous work done by this group showed that addition of 1-2% H_2 to the aerosol gas flow increased sensitivity with cryogenic desolvation two- to three-fold. It may prove worthwhile to investigate the mechanism by which this occurs. Addition of H_2 makes the central channel appear darker and wider. Since the central channel has changed, the regions of atomization and ionization have obviously changed. Addition of a molecular gas makes the plasma behave as if there was only conventional desolvation. Certainly, there is a way to determine what role the addition of hydrogen plays in this process.

Informally, it has been noted that RSDs with the membrane system are lower than those for the cryogenic system. In tuning the instrument with a solution of Li^+, Y^+, and Tl^+, RSDs using the membrane were in the range 5-10% while those using cryogenic were in the range 15-20%. Cryogenic is obviously a noisier system. Actually, turning off the magnetic stir bar that agitated the ethanol bath lowered RSDs slightly. A noise power spectrum would be useful in isolating the sources of noise.

A coworker heard at a conference that Xe^+ can be attenuated with desolvation methods. Xenon is a common impurity in the argon supply, and although the degree of impurity may vary, Xe^+ is observed in the mass spectra in all cases of desolvation.

A brief test was done to determine whether nitrogen, which is much cheaper than argon, could be used as the sweep gas. With an argon sweep gas of 1 L min^{-1}, the plasma can be easily ignited and sustained. However, with a nitrogen sweep gas of only 0.05 L min^{-1}, the plasma was difficult to ignite and could not be sustained for more than a few seconds. The plasma that did ignite had a very dark central channel. This leads to an interesting observation that the sweep gas contributes to the aerosol gas flow. It may prove interesting to monitor the argon sweep gas as it purges the membrane. The sweep gas is generally operated at a flow rate compatible with the aerosol gas flow rate to the plasma. In fact, if two ICP-MS devices were in close enough proximity, both the aerosol gas flow and the sweep gas flow could be monitored.

One of the most obvious experimental parameters to change is to lower the temperature of the cryogenic bath. Ethanol is relatively inexpensive and besides being at such a low temperature, it is relatively safe (for research purposes, of course). The first alternative one would probably think of is liquid nitrogen since it is inexpensive and easy to acquire. The boiling point of liquid N_2, however, is approximately 10°C lower than that for argon. Therefore, the argon aerosol gas will condense in the glass condenser and copper loops. Although there appears to be a temperature gradient between the low temperature bath and the aerosol in the transfer lines, liquid N_2 will condense the argon gas. Liquid oxygen, with a boiling point approximately 3°C higher than that for argon is an option, but probably not a good one since it is a terrible safety hazard. Liquid argon is also an alternative, but besides being a little more expensive, it could also condense the argon in the aerosol gas. Actually, at temperatures much lower than those achievable

with ethanol, the copper loops plug with ice.

Although both cryogenic and membrane desolvation have the same goal to remove solvent, each accomplishes that goal in a different way with a different effect observed in the plasma. Membrane desolvation has an advantage in that it has received commercial attention and so at least for the time being, cryogenic desolvation may remain a research novelty, but there are a number of things that remain to be investigated.

ACKNOWLEDGEMENTS

I am fortunate. Graduate school was not so much me learning about chemistry, but me learning about me. Nobody said it would be easy, and it wasn't. I never expect something to just be a success, but sometimes you really want to make something successful even when your best effort doesn't seem to be enough. Somewhere inside, I found the strength to continue and to make this a different success. And I owe that to many people.

A number of things shape who I am, but I credit the most to my family. We've been through a lot over the years and now I understand that much better because I've experienced it. Thanks for the sacrifices to help me get to this point, the patience, the understanding, and the support. The freedom, the ability, the willingness, and the confidence to move on and to work to make things better. For all the things I've had the opportunity to do and will have the opportunity to do. I don't think I can say or write enough.

Thanks to Dr. Sam Houk for the things that have worked out. I was really put to the test, but I wouldn't have it any other way. I had the opportunity to learn about ICP-MS from the guy who did it first. A deal like that can't be beat.

Thanks to Dr. Gary Hieftje at Indiana University to whom I attribute my start in analytical chemistry. With the "Spectrochemistry and Separations" class he taught, I was introduced to an area of chemistry that really appealed to me. His genuine interest but seriousness, a business-like no nonsense, in the subject and in teaching only enhanced the

subject matter. He invited everyone in the class to a tour of the lab, and I took him up on that offer. A few months later, after working up enough courage to ask him, he welcomed me into his group to work on a research project as an undergraduate. He was very helpful in my continuing at a quality graduate school and has continued to be a great help.

Among the good people and good friends I made in the group is Norm Sesi with whom I worked. He set a fine example as someone who worked hard and knew the importance of family. I only talked to him once since I left, but the support that he offered when I told him how things worked out was infinitely encouraging. I hope I didn't subtract too many years from his life expectancy.

Thanks to Dr. Susan Strome in the Biology Department at IU who hired me as a work-study in her lab. This was my first opportunity to work in a lab. I didn't really think of it as a job mainly because I was treated like a part of the lab. It provided a laboratory-experience foundation that I was able to build upon.

Thanks to Luis Alves from whom I inherited the cryogenic desolvation project. I only worked with Luis for about two months before he graduated, but they were very important and valuable in allowing me to begin my own research.

Thanks to the Perkin Elmer Sciex Elan 250 ICP-MS #004 with upgraded ion optics and to the Hewlett-Packard 4500 ICP-MS #3446J00151. I couldn't have done it without you guys.

Thanks to Harvey Burkholder for the rental space in the Instrumental Analysis Laboratory and for his help and patience.

Thanks to Lloyd Allen, who always had time for discussion--scientific or otherwise, for his help.

Thanks to Chris, who I've known and kept in contact with longer than anyone else and who is in a similar high-demand situation, for the occasional excursion into absurdity.

Thanks to Elmore for keeping things balanced by providing relief from the daily grind and making life more interesting.

Thanks to J. S., who may not know that I exist, but whom I'll never forget.

Thanks to Oz at the storeroom who could decipher a shopping list that read like a Dr. Seuss book with its Whatsits and Wizzits. But now that he's retired (I may be the reason), I'm sure he doesn't miss it. Thanks to Brian, Keith, Gary, and Frank at the storeroom/warehouse for their help on numerous occasions, but mainly for only charging me double on Friday afternoons.

Thanks to the Campus Police, who only needed to come to the Instrumental Analysis Lab once, for keeping things safe and secure. I still maintain that someone else set the alarm after I disarmed it earlier in the morning.

Thanks to all the people who did the little things that may have gone unpublicized, but were certainly appreciated. Especially those who showed respect and understanding in spite of my stubbornness.

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 1802 to this thesis.

CHAPTER 5. GENERAL CONCLUSION

This thesis, a continuation of previous work, has demonstrated the importance and the utility of removing solvent. Spectral interferences are generally attributed to overlapping isotopes between elements, background species, and molecular ions of matrix elements (ArO^+, $ArCl^+$, MO^+, and ClO^+). The solvent plays a key role in these spectral interferences. Certain precautions can be taken to avoid contamination, but the solvent is always present. Instrument operating conditions can be altered to lessen the effect of polyatomic ions, even the instrument itself has been altered to exclude these species. Usually, other isotopes of an element can be used to correct for a spectral interference. However, there are cases where the sample matrix complicates the mass spectrum to the extent that isotopic corrections are not possible. For this reason, it is better to remove interferences that to correct for them.

Cryogenic desolvation, a method by which solvent vapor is condensed from the aerosol stream, has demonstrated attenuation of oxide and chloride molecular ions by removing water vapor and chlorine as hydrogen chloride. Reduction of $^{35}Cl^{16}O^+$ permits the determination of $^{51}V^+$ at trace levels in a chloride matrix. The method described in Chapter 2 provides a rapid method to screen urine samples for vanadium at the 12 ppb level. Although matrix suppression and drift are corrected for by the standard ratio solution, deposition of material on the sampler and skimmer cones remains a problem. Attenuation of $^{40}Ar^{35}Cl^+$ and $^{40}Ar^{37}Cl^+$ allow this method to be extended to the determination of arsenic and selenium, respectively.