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Controlled dissolution of surface layers for elemental analysis by inductively coupled plasma-mass spectrometry

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Controlled dissolution of surface layers for elemental analysis by inductively coupled plasma-mass spectrometry

by

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Program of Study Committee:
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TABLE OF CONTENTS

GENERAL INTRODUCTION 1
References 2

CHAPTER 1 CONTROLLED DISSOLUTION OF SILICON DIOXIDE LAYERS FOR ELEMENTAL ANALYSIS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY 4
Abstract 4
Introduction 5
Experimental 7
Dissolution Procedure 7
Reagents 8
Recovery Study 8
ICP-MS Measurements 9
Results and Discussion 9
Sample Depth Removed 9
0.5% HF Results, Effect of Etch Time 10
Recovery Results 11
Effect of HF Concentration 11
Conclusion 12
Acknowledgements 12
References 12
Tables and Figures 15

CHAPTER 2 CONTROLLED DISSOLUTION OF COPPER AND BRASS LAYERS FOR ELEMENTAL ANALYSIS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY 21
Abstract 21
Introduction 22
Experimental 23
Partial Dissolution Procedure for Copper and High Copper Alloy 23
Complete Dissolution Procedure for Copper and High Copper Alloy 24
Dissolution Procedure for Brass 24
Reagents 24
ICP-MS Measurements 25
Results and Discussion 26
Sample Depth Removed 26
Copper and High Copper Alloy 26
Brass 27
Acknowledgements 28
References 28
Figures 29

GENERAL CONCLUSION 33

ACKNOWLEDGEMENTS 34

GENERAL INTRODUCTION

Determining the composition of thin layers is increasingly important for a variety of industrial materials such as adhesives, coatings and microelectronics. Secondary ion mass spectrometry (SIMS),[1-3] Auger electron spectroscopy (AES),[1-4] X-ray photoelectron spectroscopy (XPS),[1-4] glow discharge optical emission spectroscopy (GDOES),[1,3,5,6] glow discharge mass spectrometry (GDMS),[1,3,5,7] and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)[7,8] are some of the techniques that are currently employed for the direct analysis of the sample surface. Although these techniques do not suffer from the contamination problems that often plague sample dissolution studies, they do require matrix matched standards for quantification. Often, these standards are not readily available.

Despite the costs of clean hoods, Teflon pipette tips and bottles, and pure acids, partial sample dissolution is the primary method used in the semiconductor industry to quantify surface impurities. Specifically, vapor phase decomposition (VPD) coupled to ICP-MS[9-12] or total reflection x-ray fluorescence (TXRF)[13-15] provides elemental information from the top most surface layers at detection sensitivities in the 10^7-10^{10}atoms/cm^2 range.[12,15] The ability to quantify with standard solutions is a main advantage of these techniques.

Li and Houk[16] applied a VPD-like technique to steel. The signal ratio of trace element to matrix element was used for quantification. Although controlled dissolution concentrations determined for some of the dissolved elements agreed with the certified values, concentrations determined for refractory elements (Ti, Nb and Ta) were too low. LA-ICP-MS and scanning electron microscopy (SEM) measurements indicated that carbide grains distributed throughout the matrix were high in these refractory elements. These elements dissolved at a slower rate than the matrix element, Fe. If the analyte element is not removed at a rate similar to the matrix element a true representation of the sample layer cannot be realized. Specifically, the ratio of analyte signal to matrix element signal does not equal the actual ratio in the bulk sample.

The objective of this work was to investigate the controlled dissolution of other materials, simpler than steel. Matrices of copper, high copper alloy and NIST C1100 brass were investigated but the matrix that showed the best agreement between measured and certified values was NIST 612 glass. Further studies were conducted to limit the amount of surface layers removed for the NIST 612 matrix.

REFERENCES

1. J. C. Riviére, *Surface Analytical Techniques*, H. Fröhlich, P. B. Hirsch, N. F. Mott, A. J. Heeger, R. Brook, Eds. (Clarendon Press, Oxford, UK, 1990).
2. F. Adams, L. Van Vaeck, R. Barrett, Spectrochim. Acta Part B **60**, 13, (2005).
3. K. Wagatsuma, “Comparison of Glow Discharge Atomic Spectrometry with Other Surface Analysis Methods,” in *Glow Discharge Plasmas in Analytical Spectroscopy*, R.K. Marcus and J. A. C. Broekaert, Eds. (J. Wiley & Sons, Chichester UK, 2003), Ch 9.
4. F. Reniers and C. Tewell, J. Electron. Spectrosc. Relat. Phenom. **142**, 1, (2005).
5. J. Pisonero, B. Fernández, R. Pereiro, N. Bordel, A. Sanz-Medel, Trends in Analytical Chemistry **25**, 11 (2006).

6. K. Wagatsuma, “Surfaces, Thin Films and Coatings,” in *Glow Discharge Plasmas in Analytical Spectroscopy*, R.K. Marcus and J. A. C. Broekaert, Eds. (J. Wiley & Sons, Chichester UK, 2003), Ch 8.
7. M. Resano, E. García-Ruiz, M. A. Belarra, F. Vanhaecke, K. S. McIntosh, Trends in Anal. Chem. doi:10.1016/j.trac.2007.01.015 (2007).
8. J. Pisonero, J. Koch, M. Walle, W. Hartung, N. D. Spencer, D. Günther, Anal. Chem. **79**, 2325 (2007).
9. A. Krushevska, S. Tan, M. Passer, and X.R. Liu, J. Anal. At. Spectrom. **15**, 1211 (2000).
10. E. Jones Ferrero and D. Posey, J. Anal. At. Spectrom. **17**, 1194 (2002).
11. A. Danel, T. Lardin, C. Giroud, and F. Tardif, Mater. Sci. Eng. **102**, 213 (2003).
12. M. B. Shabani, Y. Shiina, F. G. Kirscht, and Y. Shimanuki, Mater. Sci. Eng. B **102**, 238 (2003).
13. D. Hellin, J. Rip, S. Arnauts, S. De Gendt, P. W. Mertens, C. Vinckier, Spectrochim. Acta Part B, **59**, 1149, (2004).
14. D. Hellin, V, Geens, I. Teerlinck, J, Van Steenbergen, J. Rip, W. Laureyn, G. Raskin, P. W. Mertens, S. De Gendt, C. Vinckier, Spectrochim. Acta Part B **60**, 209, (2005).
15. D. Hellin, S. De Gendt, N. Valckx, P. Mertens, C. Vinckier, Spectrochim. Acta Part B **61**, 496, (2006).
16. F. Li and R. S. Houk, Applied Spectroscopy, **58**, 776 (2004).

CHAPTER 1

CONTROLLED DISSOLUTION OF SILICON DIOXIDE LAYERS FOR ELEMENTAL ANALYSIS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

A paper to be submitted to *Applied Spectroscopy*

Susan Lorge and R. S. Houk

ABSTRACT

Dissolution procedures were developed to minimize the number of NIST 612 glass surface layers removed without compromising trace metal sensitivity. Varying dissolution time and hydrofluoric acid concentration resulted in the reproducible removal of SiO_2 layers approximately 70 to 500 Å deep. Dissolved trace metals were determined by high resolution inductively coupled plasma-mass spectrometry (ICP-MS). The amount removed was determined from the concentration of a major element, Ca. With the exception of Zn, trace metal concentrations agreed well with their certified values for removal depths of 500, 300 and 150 Å. Zinc concentration was significantly high in all dissolutions indicating either a contamination problem or that Zn is removed at a faster rate than Ca. For the dissolutions that removed 70 Å, Cr, Mn, Co, Sr, Cd, Ce, Dy, Er, Yb and U recovery results agreed with their true values, ~50 ppm. However, Ti, As, Mo, Ba, and Th could not be determined because net intensities were below 3 σ of the blank. Copper, Pb and Zn exhibited concentrations that were well above their true values. The high results for Cu and Pb were not pronounced in the dissolutions that removed 150 to 500 Å.

INTRODUCTION

In the semiconductor and material science industries, contamination-free surface layers are critical in the production of high performance products. The need to verify surface cleanliness has led to advances in both surface and chemical analysis techniques. Surface techniques such as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) have been improved upon for decades. To date, these techniques can provide depth resolution in the range of 5-10 Å.[1] Additionally, AES in imaging mode can offer lateral resolution (10 nm) for spatial analysis.[2]

Other surface analysis techniques that are common in laboratories that examine solid surfaces include: laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), glow discharge mass spectrometry (GDMS) glow discharge optical emission spectroscopy (GDOES) and static secondary ion mass spectrometry (sSIMS). Three of these techniques take advantage of the superior detection sensitivity and selectivity of mass spectrometry. Static SIMS can provide elemental information from a single monolayer of material.[1] The glow discharge techniques have demonstrated the potential for elemental analysis of layers less than 10 nm thick.[3,4] At present, the LA-ICP-MS depth resolution is ~0.1 µm per pulse.[3] Removal of very thin layers of surface material by LA-ICP-MS is currently being investigated by Günther et al.[5] SIMS and LA-ICP-MS can provide lateral resolution (~µm).[4,5] The glow discharge techniques cannot.

One disadvantage common among all these techniques is that quantification requires matrix matched standards. High energy ion scattering spectroscopy (high energy ISS), also known as Rutherford backscattering spectroscopy (RBS), can provide quantitative analysis without the need for matrix matched solid standards. It provides depth resolution on the order of a monolayer as well as lateral resolution.[6]

For surface analysis techniques that require a sample dissolution step such as solution ICP-MS, a procedure known as vapor phase decomposition (VPD) is employed. The vapor phase decomposition technique is popular in the semiconductor industry to extract trace metals present on silicon wafer surfaces. Briefly, the wafer is sealed in a chilled chamber and exposed to HF vapor. The surface oxide layer *(10-30 Å)* and any impurities that might be present react with the HF. Exposure time can vary from 20 minutes to 12 hours. After the oxide layer is etched, the hydrophobic silicon surface is scanned by an aqueous acid droplet (~100-500 μL) to collect the surface contaminants.[7] An evaporation step will often follow to remove most of the silicon and fluoride as volatile SiF_4. The concentrations of metal contaminants in the final solution can then be determined by TXRF or ICP-MS. Optimization of VPD-ICP-MS[7-10]and VPD-TXRF [11-13] have been described elsewhere. The ability to quantify trace elements with the use of standard solutions is a clear advantage of these techniques. However, providing a clean environment for sample preparation is costly.

Li and Houk[14] modified the vapor phase decomposition method in an effort to apply this powerful controlled dissolution technique to steel. Quantification was done relative to the major element, Fe. Problems arose when some of the trace element concentrations did not correspond to the certified concentrations. Elements like Ti, Nb and Ta, gave low results for the controlled dissolution which indicated that these elements dissolved more slowly than the Fe. Further LA-ICP-MS and scanning electron microscopy (SEM) experiments determined that these problem elements were associated with refractory carbide grains distributed throughout the Fe matrix.

It is believed that trace metals homogeneously distributed throughout the matrix would have uniform removal rates. At the start of this study, various simpler matrices than steel were investigated.[15] NIST 612 glass was found to work best. Efforts were made to limit the amount of surface dissolved while still removing enough material to determine the trace metals.

EXPERIMENTAL

Dissolution Procedure. As shown in Figure 1.1, a cylindrical hole (5 mm diameter, ~0.5 mm depth) was diamond cut into a glass wafer to hold the etch solution for partial dissolution. The sample was a glass standard reference material (NIST 612, Trace Elements in Glass) with nominal trace element concentrations of 50 mg/kg (ppm). The same sample was etched repeatedly for fixed times with an etch solution (2 μL) that evenly coated the bottom of the hole. After a five or ten second waiting period, a wash of dilute HNO_3 (4 μL) was transferred into the hole. The etch solution and wash solution were then withdrawn and diluted to 1 mL with more wash solution. Etches were performed on separate days. Each day three replicate samples were prepared.

All sample preparation was carried out in a clean hood (Class 100, Design Filtration Inc.) to reduce sample contamination. Teflon bottles (FEP, Nalge Nunc Int.) were acid vapor washed with nitric acid (~70%) for at least 24 hours prior to use. Teflon pipette tips (PFA, Elemental Scientific Inc.) were soaked in 5% HNO_3 overnight. These cleaned bottles and pipette tips were rinsed with deionized water (18.2 MΩ, Millipore) and allowed to dry before use.

Reagents. Fuming nitric acid and concentrated hydrofluoric acid (ULTREX II, JT Baker) were further purified by in-house sub-boiling distillation. The acids underwent a minimum of two cycles (four half turns) inside Teflon stills (Savillex). The etch solutions had HNO_3 at 1% in deionized water with HF at 0.1, 0.25 or 0.5%. The etch solution was prepared daily. The wash solution was 0.1% HNO_3 in deionized water. A multielement standard with concentrations of 1 ppb As, Ba, Cd, Cr, Co, Cu, Mn, Mo, Pb, Sr, Zn (Varian, 50 mg/L) Ce, Dy, Er, Ru, Th, Ti, U, Yb (PlasmaCHEM, 1000 mg/L) and 10 ppb Ca and Ir (PlasmaCHEM, 1000 mg/L) was prepared weekly. Ir and Ru were the internal standards used for quantification for Ca and the trace elements, respectively. All standards were prepared in the same solution matrix as the samples. Trace element concentrations in the solid were related back to the major element concentration, Ca, to reflect the overall composition of the solid.

Recovery Study. The dissolution procedure was performed on pure quartz glass to evaluate the reproducibility of handling sub-ppb solutions cleanly. The diamond cut hole (5 mm diameter, ~0.5 mm depth) was cleaned with 10 µL of etch solution. A blank was then prepared using the dissolution procedure described previously for 10 and 5 seconds with an etch acid of 0.5% HF in 1.0% HNO_3. The hole was then spiked with 5 µL of 100 ppb multielement solution and allowed to dry in the clean hood. The residue was re-dissolved in 0.5% HF in 1% HNO_3, as if the metals came from the quartz. These samples were diluted so that the recovered trace metals would be at a concentration of ~0.25 ppb.

ICP-MS Measurements. A magnetic sector instrument (Finnigan, Element 1) was used in medium resolution ($m/\Delta m = 4000$) for all experiments. A PFA pneumatic nebulizer (PFA-100, Elemental Scientific, Inc., sample uptake 100 µL/min) and a Teflon, Scott-type, double-pass spray chamber (ESI) were used for sample introduction. Platinum tipped sampler and skimmer cones were used due to the inert properties of platinum in the presence of HF. ICP operating conditions were adjusted to maximize signals for ^{7}Li, ^{115}In and ^{238}U at a forward power of 1200W. The detector remained in counting mode for all experiments. The ^{44}Ca isotope was monitored because of the few polyatomic interferences. The mass spectrometer was operated under electrostatic scanning conditions (mass window 150%, 20 samples per peak, 16 runs per sample, sample time 0.01 s).

RESULTS AND DISCUSSION

Sample Depth Removed. The depth of sample removed is estimated as follows using values measured from a 10 s etch. Using the measured signals for Ca and the internal standard, the volume of the etch solution, and the Ca concentration (8.57%) in the sample, the approximate amount of Ca removed is 2.30 µg. Dividing by the density of the NIST glass (2.36 g/cm^3), the volume of the solid removed is ~0.001 mm^3. The area of the hole is 20 mm^2, so the depth removed for the 10 s etch is approximately 500 Å, or 330 atomic layers. Calculations are based on the assumption that the glass is being etched straight down. Decreasing etch time and etch acid concentration decreases the amount of sample removed.

0.5% HF Results, Effect of Etch Time. Comparisons of measured and certified concentrations[16] for the removal of 500 (0.5% HF, 10 s) and 300 Å (0.5% HF, 5 s) are shown in Figures 1.2 and 1.3, respectively. In both figures the Zn concentration is high; it appears to be removed at a significantly faster rate than the other elements. This is a recurring trend throughout all dissolutions. Upon closer examination of the 10 s data, the Zn concentrations in the solid are twice their true values for seven out of the 11 samples. The remaining four show Zn concentrations that are eight to ten fold too high. Three of these four very high values were taken on the same day. The 5 s etch data (Figure 1.3) shows worse precision with five out of nine Zn concentrations that are 15-20 times higher than their true values. The four Zn concentrations that do not follow this trend include three that are 25-40 times higher and a single concentration that showed an increase of six fold. A surface contamination problem is unlikely because the same hole was etched repeatedly. Four isotopes of zinc were included in the method, all four isotopes gave the same high result every time. Thus, spectral interferences on Zn are not the problem. The standard reduction potential of Zn is similar to that of Cr but this element does not exhibit an inordinately fast removal rate. Contamination from etch acid and pipette tips would have been observed for in the blank. The bottles were checked for high Zn levels. The zinc standard used to make the multielement solution was compared to a second zinc standard to ensure that the standard itself was not contaminated.

Although agreement is better for the other elements, it could be conceived that the removal rates for all the elements are not uniform. If we assume the errors in etch time and pipette volume are the same for all dissolution steps, variations in the error bars should be minimal. However, this is not the case. Arsenic, Cu, Cr, Mo and Ti have uncertainties that fall in the range of 20-50%. Cu and Cr are common components of dust.[17] Although all sample preparation was completed in the clean hood, analysis of the sample is done outside of the clean hood. Care was taken to cap the bottle during sample introduction, but a single dust particle can cause significant contamination at parts per trillion concentrations. The remaining elements have standard deviations that are 15% or better.

Recovery Results. Recovery data on quartz glass is presented in Table 1.1. It is shown that most elements have acceptable recovery results between 75 and 100%. The results for the 10 s etch are lower than the results for the 5 s etch but this is within the standard deviations of day to day results in the NIST 612 recovery experiments. It is interesting to note that the recovery results for Zn are not significantly high for this study. Since the same sample preparation environment and the same cleaning techniques for the acids, bottles and pipette tips were used in both the NIST 612 and the quartz dissolutions, contamination from these sources is not considered a big problem. This further weakens the argument that the high result for zinc is attributed to contamination. It is also evident from the quartz recoveries that these small amounts can be handled reproducibly.

Effect of HF Concentration. In addition to time, it is possible to regulate the amount of sample removed by varying HF concentration. All recovery results, except Zn, are within the range of 80-140% for the removal of 150 Å (0.25% HF, 5 s) as shown in Figure 1.4. The net intensities for Ti were lower than 3σ of the blank despite repeated attempts to improve its detection limit. Titanium is an element that requires HF to remain oxidized in solution. The lower concentration of HF in the final solution could account for its low sensitivity. For the removal of 70 Å (0.1% HF, 5 s) as shown in figure 1.5, the limitation of this experiment has been reached. About half the elements are removed at about the same rate as the matrix element. The remaining elements have net intensities lower than 3σ of the blank.

CONCLUSION

The use of this controlled dissolution method to determine trace metal concentrations from thin solid layers is reliable for removal depths of 300 Å or more. Zinc is shown to be a problem element for all dissolutions. For removal depths of 150 Å, Ti was below the detection limit for all attempts. Removal of 70 Å or less can be done but sensitivity for about half of the trace elements observed will be compromised. For the elements that could be quantified, their removal rates were comparable to the matrix element except for Zn and Cu. It appears that the limit of this technique has been reached.

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REFERENCES

1. F. Adams, L. Van Vaeck, R. Barrett, Spectrochim. Acta, Part B, **60**, 13 (2005).
2. F. Reniers and C. Tewell, J. Electron. Spectrosc. Relat. Phenom., **142**, 1 (2005).
3. M. Resano, E. Garcia-Ruiz, M. A. Belarra, F. Vanhaecke, K. S. McIntosh, Trends Anal. Chem. doi:10.1016/j.trac.2007.01.015 (2007).

4. J. Pisonero, B. Fernández, R. Pereiro, N. Bordel, A. Sanz-Medel, Trends in Analytical Chemistry **25**, 11 (2006).
5. J. Pisonero, J. Koch, M. Walle, W. Hartung, N. D. Spencer, D. Günther, Anal. Chem. **79**, 2325 (2007).
6. K. Wagatsuma, "Comparison of Glow Discharge Atomic Spectrometry with Other Surface Analysis Methods," in *Glow Discharge Plasmas in Analytical Spectroscopy*, R.K. Marcus and J. A. C. Broekaert, Eds. (J. Wiley & Sons, Chichester UK, 2003), Ch 9.
7. A. Krushevska, S. Tan, M. Passer, and X.R. Liu, J. Anal. At. Spectrom. **15**, 1211 (2000).
8. E. Jones Ferrero and D. Posey, J. Anal. At. Spectrom. **17**, 1194 (2002).
9. A. Danel, T. Lardin, C. Giroud, and F. Tardif, Mater. Sci. Eng., **102**, 213 (2003).
10. M. B. Shabani, Y. Shiina, F. G. Kirscht, and Y. Shimanuki, Mater. Sci. Eng., B **102**, 238 (2003).
11. D. Hellin, J. Rip, S. Arnauts, S. De Gendt, P. W. Mertens, C. Vinckier, Spectrochim. Acta Part B, **59**, 1149, (2004).
12. D. Hellin, V, Geens, I. Teerlinck, J, Van Steenbergen, J. Rip, W. Laureyn, G. Raskin, P. W. Mertens, S. De Gendt, C. Vinckier, Spectrochim. Acta Part B **60**, 209, (2005).
13. D. Hellin, S. De Gendt, N. Valckx, P. Mertens, C. Vinckier, Spectrochim. Acta Part B **61**, 496, (2006).
14. F. Li and R. S. Houk, Applied Spectroscopy, **58**, 776 (2004).
15. S. Lorge, M.S. Thesis, Iowa State University, Ames, IA (2007), Ch. 2.

16. N. J. G. Pearce, W. T. Perkins, J. A. Westgate, M. P. Gorton, S. E. Jackson, C. R. Neal, and S. P. Chenery, Geostandards Newsletter: The Journal of Geostandards and Geoanalysis, **21**, 115 (1997).
17. R. Richter, *Clean Chemistry: Techniques for the Modern Laboratory* (Milestone Press, CT, 2003).

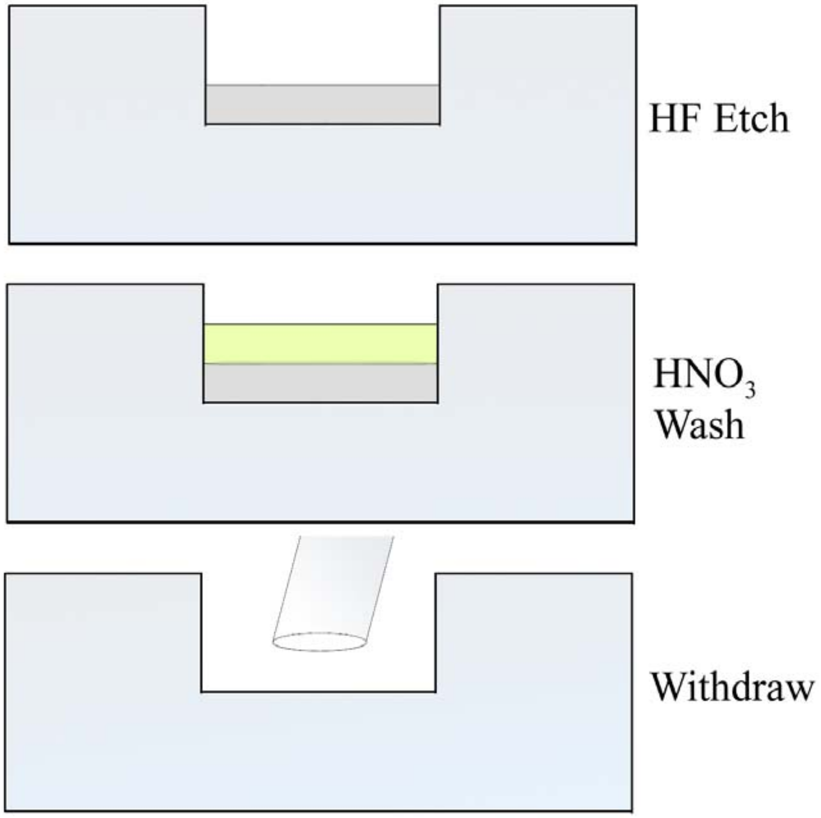

Figure 1.1 Illustration of the controlled dissolution set up for the etching of the glass sample.

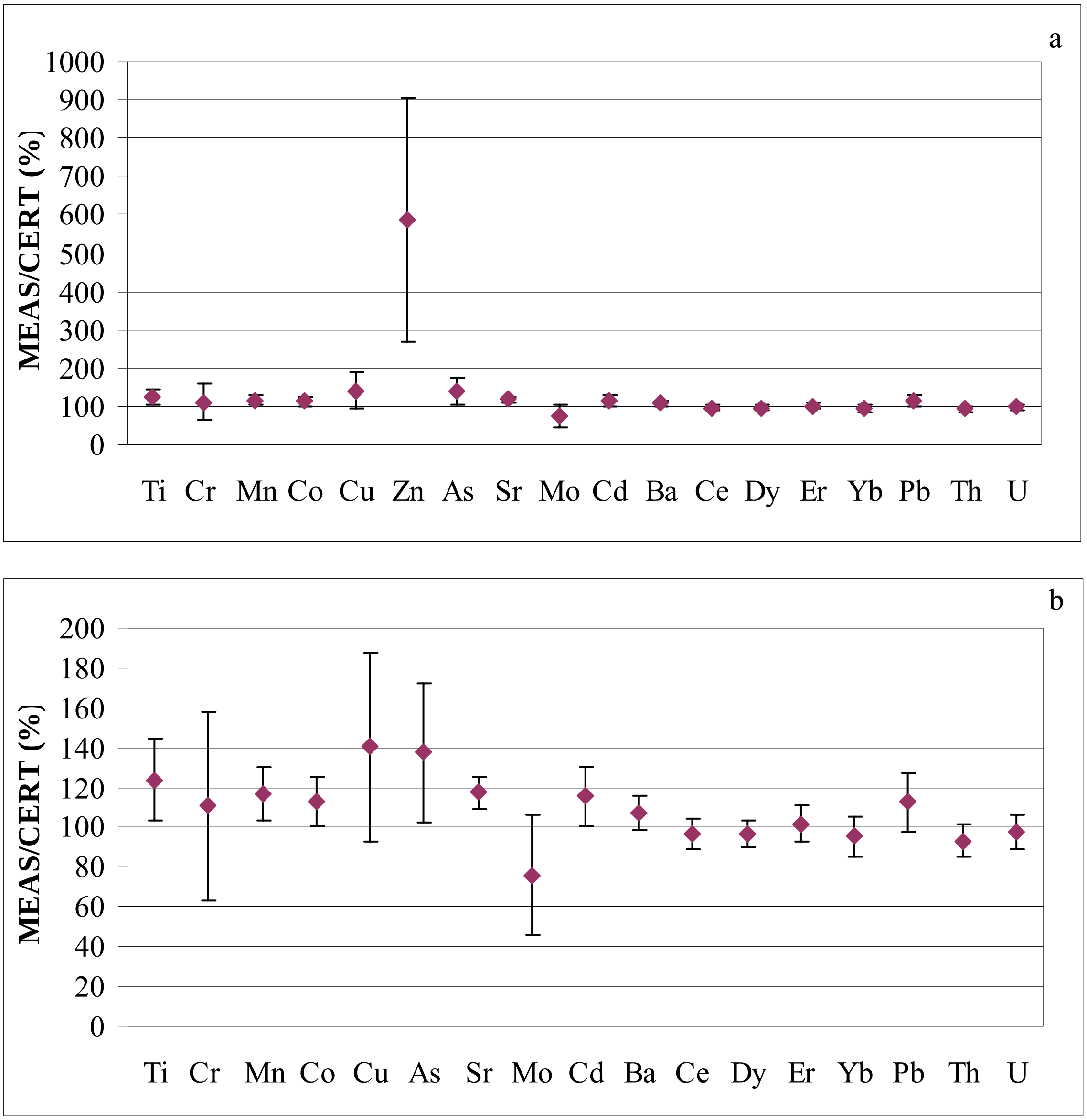

Figure 1.2 Comparison of measured and certified concentrations for (a) all elements investigated and for (b) all elements investigated except Zn in NIST 612 glass. The etch volume is 2.0 µL. The etch time is 10 seconds. The etch solution is 0.5% HF 1.0% HNO_3. Error bars are for n = 6 to 11 separate measurements.

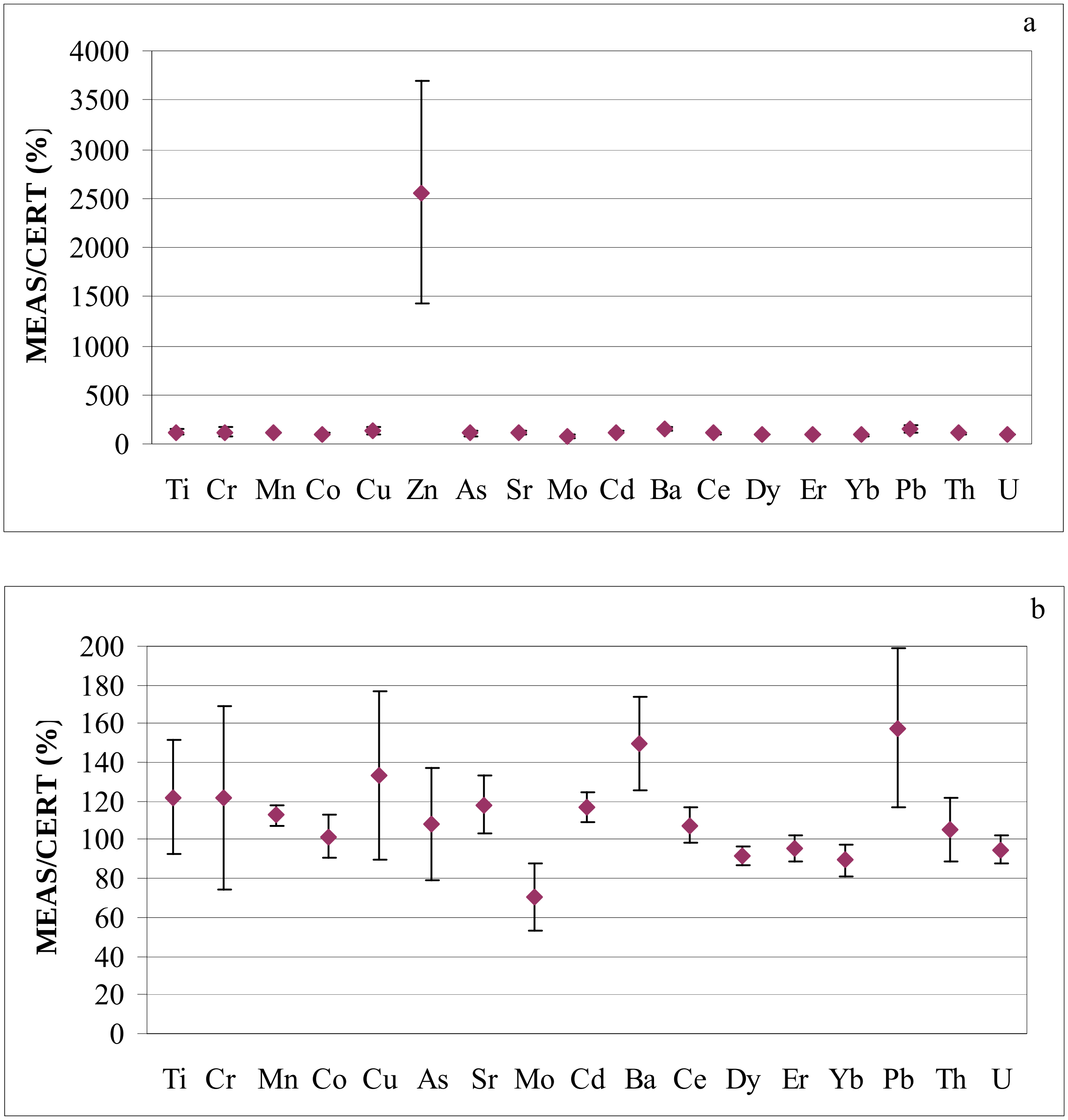

Figure 1.3 Comparison of measured and certified concentrations for (a) all elements investigated and for (b) all elements investigated except Zn in NIST 612 glass. The etch volume is 2.0 µL. The etch time is 5 s. The etch solution is 0.5% HF 1.0% HNO_3. Error bars are for n = 9 separate measurements.

Table 1.1 Recovery of trace metals from quartz glass surface

	Recovery (%)	
Element	**10s**	**5s**
Ti	82	76
Cr	60	81
Mn	81	108
Co	79	100
Cu	96	114
Zn	89	109
As	68	95
Sr	82	94
Mo	74	80
Cd	87	94
Ba	76	92
Ce	78	94
Dy	83	105
Er	85	98
Yb	90	106
Pb	84	101
Th	67	77
U	90	106

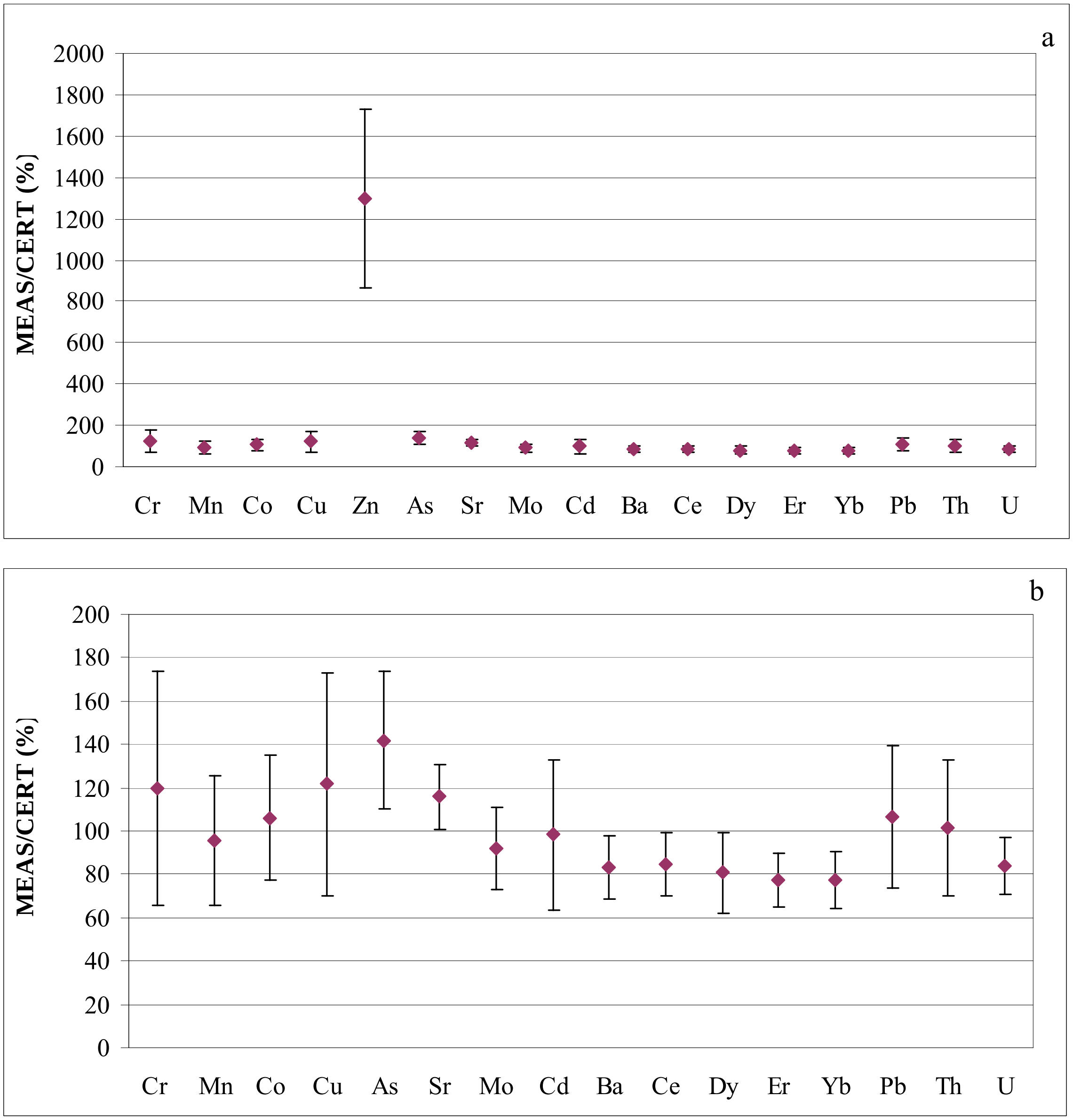

Figure 1.4 Comparison of measured and certified concentrations for (a) all elements investigated and for (b) all elements investigated except Zn in NIST 612 glass. The etch volume is 2.0 µL. The etch time is 5 s. The etch solution is 0.25% HF 1.0% HNO_3. Error bars are for n = 4 to 9 separate measurements.

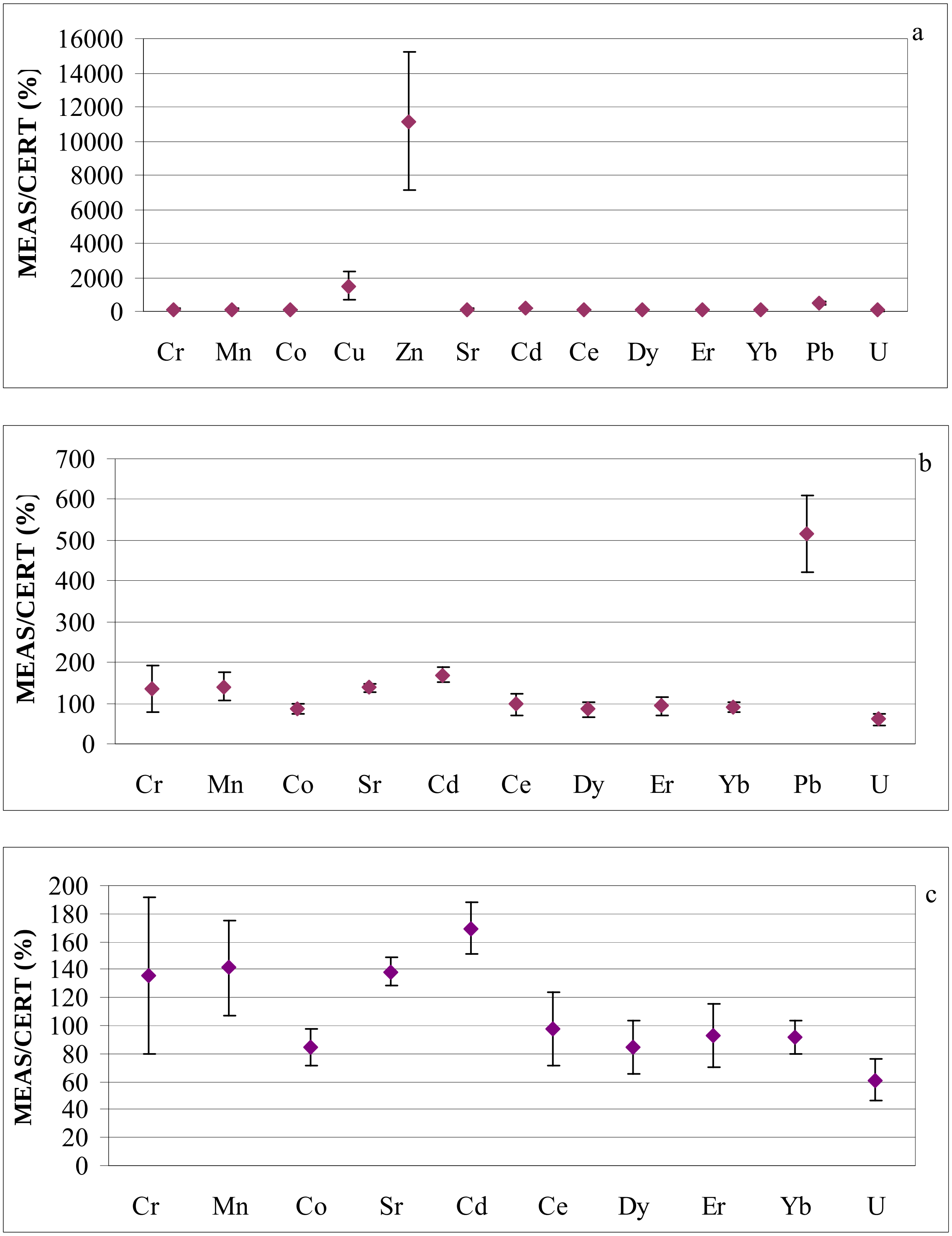

Figure 1.5 Comparison of measured and certified concentrations for (a) all elements investigated (b) all elements investigated except Zn and Cu (c) all elements investigated except Zn, Cu and Pb in NIST 612 glass. The etch volume is 2.0 µL. The etch time is 5 seconds. The etch solution is 0.10% HF 1.0% HNO_3. Error bars are for n = 5 to 9 separate measurements.

CHAPTER 2

CONTROLLED DISSOLUTION OF COPPER AND BRASS LAYERS FOR ELEMENTAL ANALYSIS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

Susan Lorge and R. S. Houk*

ABSTRACT

Copper, high copper alloy and NIST C1100 brass samples are partially dissolved to determine whether trace metals are removed at the same rate as the major element. Dissolved trace metals are determined by inductively coupled plasma-mass spectrometry (ICP-MS) using a magnetic sector instrument. Varying nitric acid concentration and etch time showed the removal of sample layers of the following depths: 2700 and 2500 Å for the copper, 2000 and 1800 Å for the high copper alloy, and 150 and 100 Å for the brass. The amount of material removed is determined from a major element. Trace metal concentrations were measured relative to the concentration of a major element in the solutions to reflect the overall sample composition. Since the copper and the high copper alloy samples did not have certified concentration values, complete dissolutions were also needed. The partial dissolution concentrations were higher than complete dissolution concentrations for most trace metals. This observation indicates that either the trace metals are removed at a faster rate than the matrix element or that the trace elements are not homogeneous with depth in the sample.

INTRODUCTION

Elemental analysis of thin solid layers is important in the semiconductor and material science industries. X-ray photoelectron spectroscopy (XPS), auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS) are the classical techniques employed for this purpose. They can provide elemental information from a single monolayer of material.[1] Although the previously mentioned techniques are more common, glow discharge (GD) coupled to optical emission spectroscopy (OES) and mass spectrometry (MS) has shown some promise for elemental analysis of thin films (less than 10 nm thick).[2] These processes do not require the need for sample dissolution but matrix matched standards are needed for quantification.

Controlled dissolution of samples followed by ICP-MS[3-6] or TXRF[7-9] is often used to provide quantitative analysis of surface layers in some materials. Vapor phase decomposition is the primary controlled dissolution method for trace metal determination in the semiconductor industry. The process involves the etching of SiO_2 layers and any impurities that are present in those layers with concentrated HF vapor. After an exposure times of 20 minutes to 12 hours, the resulting hydrophobic silicon surface is reproducibly scanned by an aqueous acid droplet (~100 μL) to collect the condensate.[3] The analytical environment must be carefully controlled to prevent contamination.

Sample heterogeneity presents a problem for the quantification of thin solid layers. This is evident in the work done by Li and Houk[10] in which concentrations determined from the controlled dissolution of steel were lower than the certified values for several elements (Ta, Nb and Ti). Laser ablation-inductively couple plasma-mass spectrometry (LA-ICP-MS) and scanning electron microscopy (SEM) measurements indicated that these elements were localized in small refractory grains throughout the matrix.

As a result of the study by Li and Houk[10], it was believed a simpler matrix would provide more uniform removal rates for trace metal quantification. In this study efforts were made to investigate the removal rates of trace elements from copper, high copper alloy and brass.

EXPERIMENTAL

Partial Dissolution Procedure for Copper and High Copper Alloy. As shown in Figure 2.1, a hole (5 mm diameter, ~5 mm depth) was bored into the metal to hold the etch solution. Pure copper and high copper alloy (Ames Laboratory machine shop) with trace metal concentrations of 0.02 to 4 mg/kg (ppm) and 0.1 to 50 mg/kg (ppm) were used. The partial dissolution concentrations were compared with the complete dissolution concentrations to compare the rate at which metals are removed from the surface. The same sample was etched repeatedly and the trace metals determined. A fresh sample surface was prepared each time by transferring 10 µL of concentrated aqueous HNO_3 into the hole, rinsing with deionized water and drying. The etch acid (8 µL, 10% HNO_3) was then added. After 5 or 10 seconds, the etch acid was withdrawn and diluted to 1 mL with 0.1% HNO_3. The trace metals were determined for three replicate samples of the Cu and the Cu alloy. After trace metal determination, the solution was diluted further by a factor of 100 to determine the concentration of the major element, Cu, in the partial dissolution.

Complete Dissolution Procedure for Copper and High Copper Alloy. The hole shown in Figure 2.1 was cut out for complete dissolution. The masses of the Cu and the high Cu alloy were 0.8245 and 0.4346 g, respectively. The pieces were dissolved in 10 mL of concentrated aqueous nitric acid. Fifteen microliters of this solution was diluted to 10 mL with 0.1% HNO_3 to determine the trace elements. Ten microliters of the trace element solution was diluted to 100 mL to measure the Cu.

Dissolution Procedure for Brass. A hole (~5 mm diameter, ~5 mm depth) was bored into the metal sample to hold the etch solution for partial dissolution. The sample was a brass standard reference material (NIST C1100) with trace element concentrations that range from 0.001 to 0.106 wt. % and major element concentrations of 67.4 and 32.2 wt. % for Cu and Zn, respectively. Since Zn could be monitored using ^{66}Zn (27.90%) at the same dilution as the trace metals, its concentration was determined instead of Cu. Ten microliters of etch solution (1% or 5% nitric acid) evenly coated the bottom of the hole. After 10 seconds, the etch solution was withdrawn and diluted to 1 mL with the 0.1% HNO_3.

Reagents. Fuming nitric acid (~70 %, ULTREX II, JT Baker) was further purified by in-house sub-boiling distillation. The batch was distilled a minimum of four times before the acid was used. For the copper and high copper alloy etch solution, fuming nitric acid was diluted with deionized water (18.2 MΩ, Millipore) to 10 % HNO_3. For the brass etch solution, fuming nitric acid was diluted with deionized water to 1 and 5%. The etch solution was prepared daily. Fuming nitric acid was diluted with deionized water to 0.1% HNO_3 to use for solvent in all dilutions.

For the copper and high copper alloy dissolutions, a multielement standard solution with concentrations of 1 ppb Ag, As, Bi, Cd, Cr, Ga, Pb, Sr, Zn (PlasmaCHEM, 1000 mg/L) and 10 ppb Cu and In (PlasmaCHEM, 1000 mg/L) was prepared weekly. Ga and In were the internal standards used for quantification. For the brass dissolutions, a multielement standard with concentrations of 1 ppb Be, Al, Si, Mn, Fe, Ni, Zn, As, Ag, Cd, Sn, Ir, Pb was prepared weekly. Ir was the internal standard used for quantification. All standards were prepared with the same solution matrix as the samples. Trace element concentrations in the solid were related back to the major element concentration to reflect the overall composition of the solid.

ICP-MS Measurements. A magnetic sector instrument (Finnigan Element 1) was used in medium resolution ($m/\Delta m = 4000$) for all experiments. A PFA pneumatic nebulizer (PFA-100, Elemental Scientific, Inc., sample uptake100 μL/min) and a Teflon, Scott-type, double-pass spray chamber (ESI) were used for sample introduction. Platinum tipped sampler and skimmer cones were used. ICP operating conditions were optimized to maximum signal for ^{7}Li, ^{115}In and ^{238}U at a forward power of 1200 W. The minor isotopes of the major elements were monitored so that the detector could remain in counting mode for all experiments. The mass spectrometer was operated under electrostatic scanning conditions (mass window 150%, 20 samples per peak, 16 runs per sample, sample time 0.01 s).

RESULTS AND DISCUSSION

Sample Depth Removed. The depth of sample removed for the partial dissolution of copper and high copper alloy is estimated as follows. Using the concentration determined from the internal standard and the volume of the etch solution the approximate amount of Cu removed is 39.8 μg. Dividing by the density of copper (8.920 g/cm^3), the volume of the solid removed is ~0.004 mm^3. The area of the hole is 20 mm^2, so the depth removed for the 10 s etch is approximately 2000 Å, or 800 atomic layers. For C1100 brass (32.2% Zn), the approximate amount of Zn removed is 1.90 μg. Dividing by the density of the brass (8.326 g/cm^3), the volume of the solid removed is ~2x10^{-4} mm^3. The area of the hole is 20 mm^2, so the depth removed for the 10s etch is approximately 100 Å, or 50 atomic layers. These calculations are based on the assumption that the samples are being etched straight down. If undercutting occurs, fewer layers would be removed than indicated by these estimates. Decreasing etch time or etch acid concentration decreases the amount of sample removed.

Copper and High Copper Alloy. Comparisons of partial and complete dissolution concentrations for the removal of 2500 Å Cu (5s), 2700 Å Cu (10s), 1800 Å high Cu alloy (5s) and 2000 Å high Cu alloy (10s) are shown in Figures 2.2 and 2.3, respectively. Elements whose net signals are above 3 σ of the blank are shown. For the removal of 2000 Å, Pb concentrations determined from the partial dissolutions agree with those determined for the complete dissolutions. This agreement would indicate that Pb dissolves at about the same rate as the Cu matrix. However, partial dissolution concentrations that are two to four times higher than complete dissolution concentrations are found for Pb at removal depths of 1800, 2500, and 2700 Å. At all removal depths, the

Cd, Cr, Zn, and Sr concentrations determined for the partial dissolutions were significantly higher than those for the complete dissolutions. This disagreement indicates that either the trace metals are removed at a faster rate than the Cu matrix atoms or that there is an inhomogeneous distribution of trace metals throughout the sample.

Brass. Comparisons of measured and certified concentrations for the removal of 150 Å (5% HNO_3) and 100 Å (1% HNO_3) are shown in Figures 2.4 a and b, respectively. For the removal of 150 Å, partial dissolution concentrations agree well with the certified value for Mn, Ni and Cd. Apparently, these metals are removed at about the same rate as the reference element, Zn. Iron, As, Pb and Bi show partial dissolution results that are two to seven times higher than the certified values. Apparently, these elements are removed at a faster rate than the major component Zn. For the removal of 100 Å, Ni, Cd and Sn show removal rates similar to Zn. Aluminum, Mn, Fe, As, Pb and Bi are removed at a faster rate than Zn. For Ag, the concentrations determined from the partial dissolution are lower than the certified values, indicating that this element dissolves more slowly than Zn.

Compared to the copper and high copper alloy results, the more metals detected and the better agreement between measured and certified values shown in this brass sample are probably attributed to the higher concentration and more homogeneous distribution of trace metals in the original sample and to the fewer dilution steps needed for quantification.

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REFERENCES

1. F. Adams, L. Van Vaeck, R. Barrett, Spectrochim. Acta Part B **60**, 13, (2005).
2. J. Pisonero, B. Fernández, R. Pereiro, N. Bordel, A. Sanz-Medel, Trends in Analytical Chemistry **25**, 11 (2006).
3. A. Krushevska, S. Tan, M. Passer, and X.R. Liu, J. Anal. At. Spectrom. **15**, 1211 (2000).
4. E. Jones Ferrero and D. Posey, J. Anal. At. Spectrom. **17**, 1194 (2002).
5. A. Danel, T. Lardin, C. Giroud, and F. Tardif, Mater. Sci. Eng. **102**, 213 (2003).
6. M. B. Shabani, Y. Shiina, F. G. Kirscht, and Y. Shimanuki, Mater. Sci. Eng. B **102**, 238 (2003).
7. D. Hellin, J. Rip, S. Arnauts, S. De Gendt, P. W. Mertens, C. Vinckier, Spectrochim. Acta Part B, **59**, 1149, (2004).
8. D. Hellin, V, Geens, I. Teerlinck, J, Van Steenbergen, J. Rip, W. Laureyn, G. Raskin, P. W. Mertens, S. De Gendt, C. Vinckier, Spectrochim. Acta Part B **60**, 209, (2005).
9. D. Hellin, S. De Gendt, N. Valckx, P. Mertens, C. Vinckier, Spectrochim. Acta Part B **61**, 496, (2006).
10. F. Li and R. S. Houk, Applied Spectroscopy, **58**, 776 (2004).

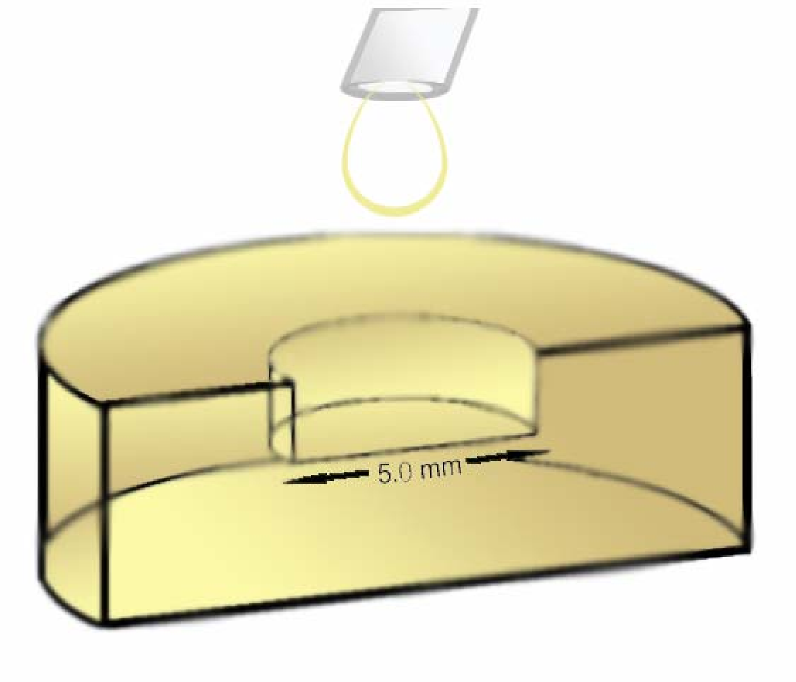

Figure 2.1 Illustration of the controlled dissolution set up for the etching of the copper, high copper alloy and NIST C1100 brass samples.

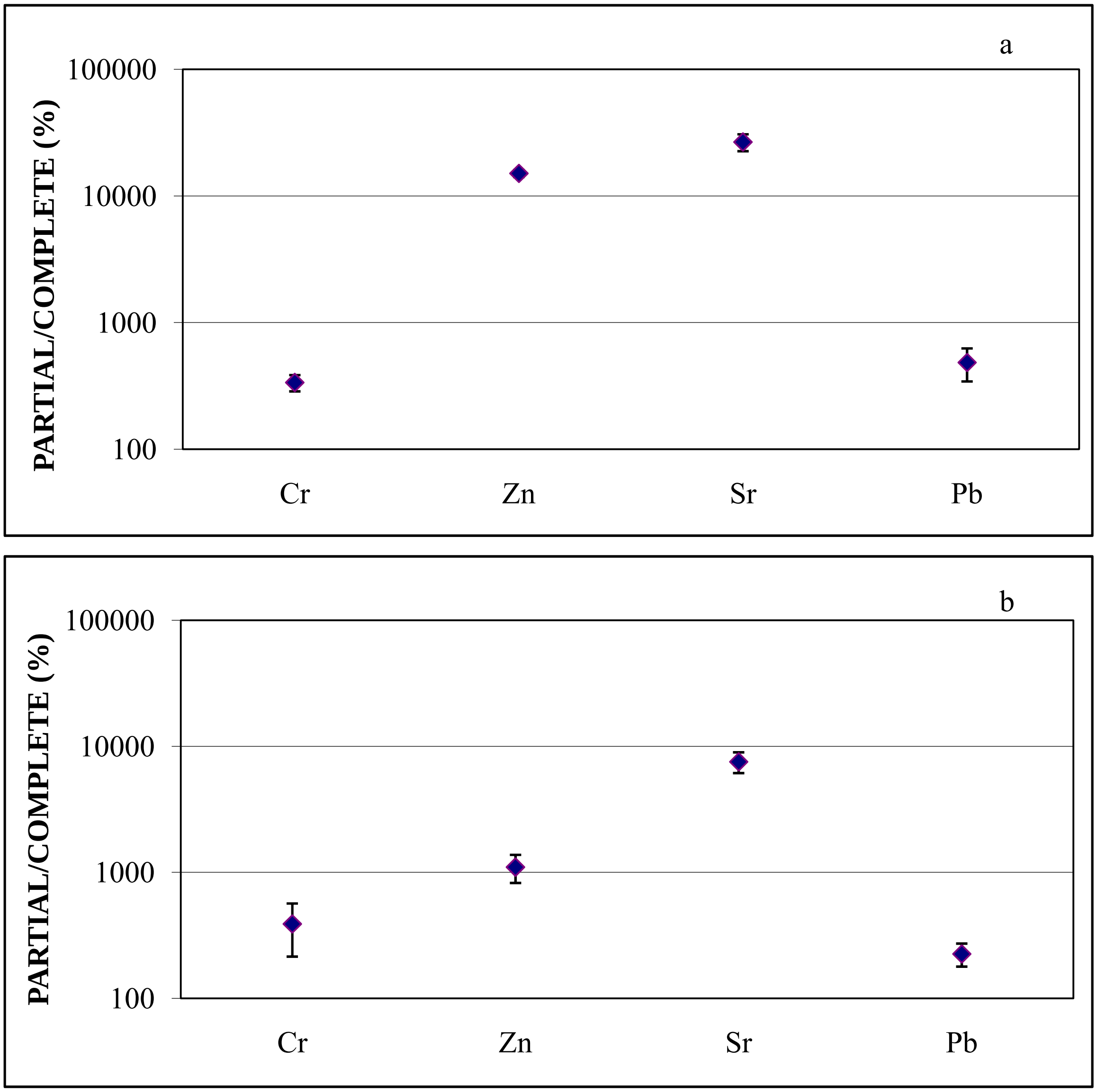

Figure 2.2 Comparison of partial and complete dissolution concentrations for elements detected in copper at etch times of (a) 5 and (b) 10 seconds. The etch volume is 8.0 µL. The etch solution is 10.0% HNO_3. Error bars are for n = 5 to 8 separate partial dissolution measurements and n = 3 separate dissolution measurements. Note change to logarithmic scale.

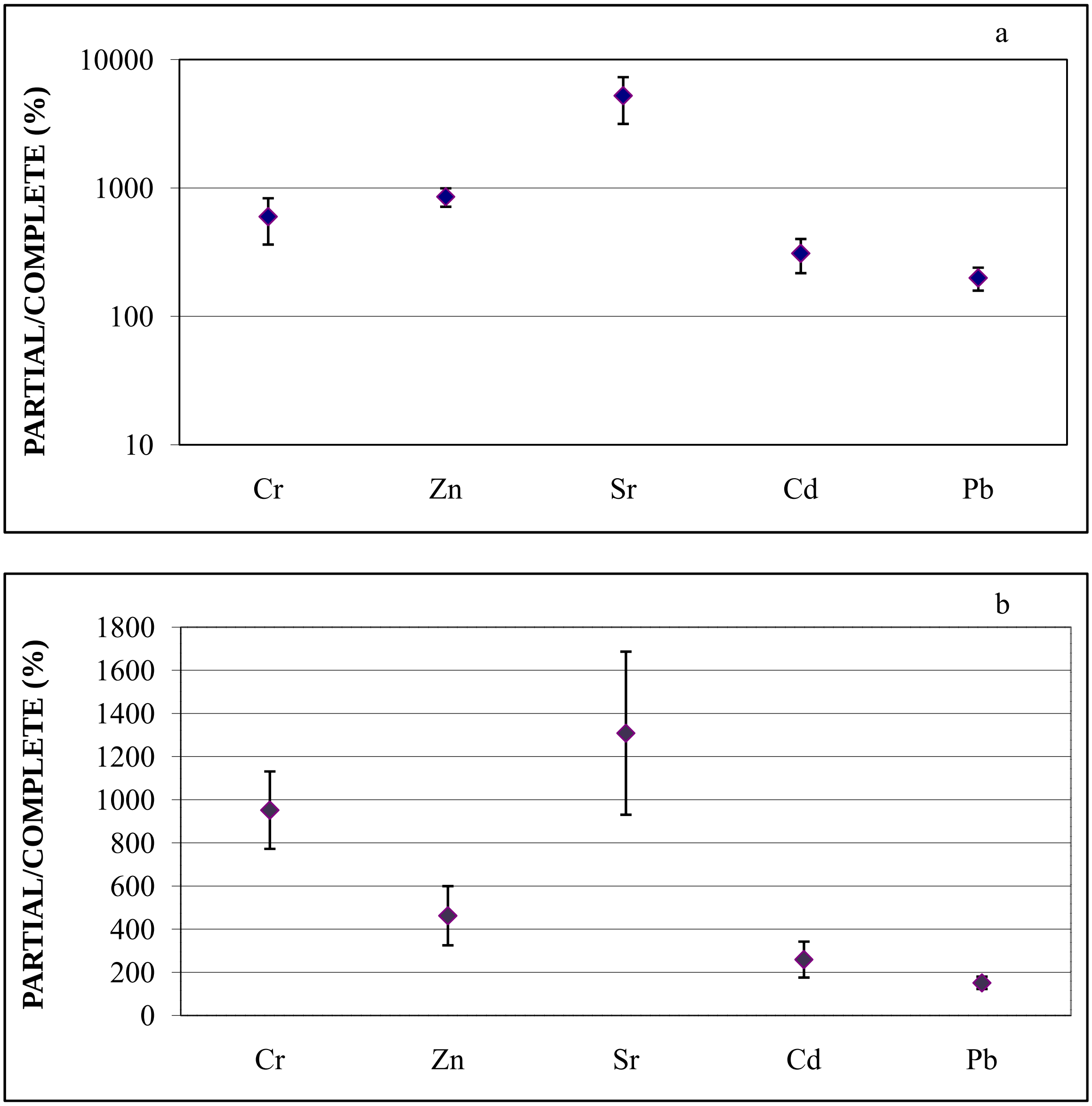

Figure 2.3 Comparison of partial and complete dissolution concentrations for elements detected in the high copper alloy at etch times of (a) 5 and (b) 10 seconds. The etch volume is 8.0 µL. The etch solution is 10.0% HNO_3. Error bars are for n = 5 to 9 separate partial dissolution measurements and n = 3 separate complete dissolution measurements. Note change to logarithmic scale in (a).

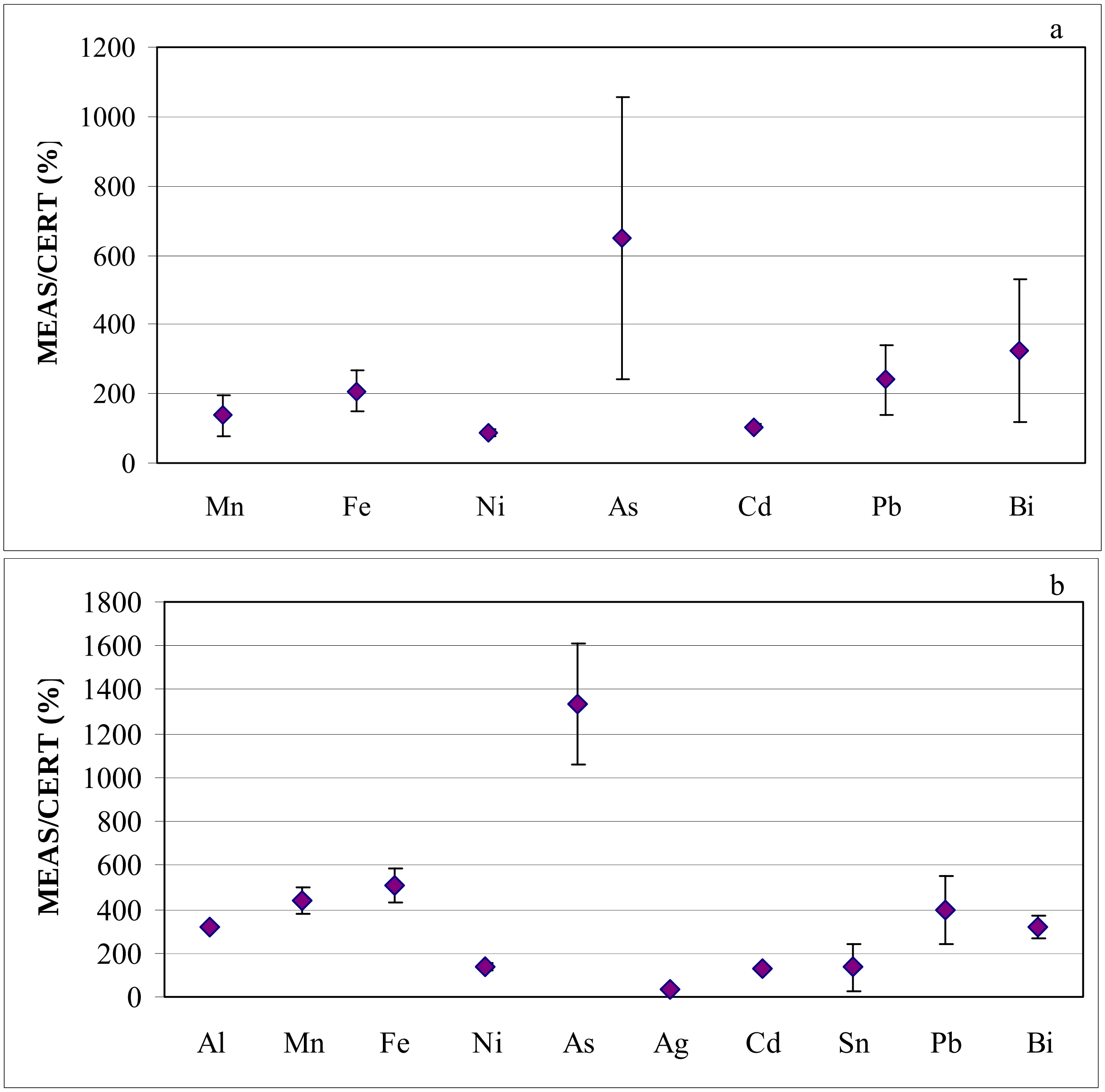

Figure 2.4 Comparison of measured and certified concentrations for elements detected in Brass C1100 at etch acid concentrations of (a) 5% and (b) 1% HNO_3. The etch volume is 10.0 µL. The etch time is 10 seconds. Error bars are for n = 3 to 6 separate measurements.

GENERAL CONCLUSION

The focus of this work was to use a controlled dissolution procedure to determine the elemental composition of surface layers. The concentration of trace elements whose removal rates are comparable to the major element removal rate can be determined accurately. Conversely, removal rates which are not consistent with the major element removal rate result in a misrepresentation of the trace metal concentration in the sample. For the copper, high copper alloy and NIST C1100 brass matrices, the partial dissolutions gave an overrepresentation for most of the trace metals present in the sample. No optimization was done on theses matrices because too few elements shared the same removal rate as the matrix element. NIST 612 glass provided a sample matrix in which trace metal concentrations, with the exception of zinc, could be determined from the partial dissolution alone at removal depths of 300 Å or more. With lower acid concentration and etch time, the amount of sample removed was reduced to 70 Å, however, half the elements had net intensities lower than 3 σ of the blank.

Future work would include an attempt to remove fewer than 70 Å with a lower acid concentration. The sample would need to be diluted less extensively. However, this may lead to matrix effect issues. Also, a look at the removal of trace metals from other oxide matrices may be of some interest.

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