Part-per-Quadrillion (PPQ) Analysis of Ultrapure Deionized Water for Semiconductor Fabs

By Dr. Hugh Gotts and David Bollinger

Abstract

Decreasing impurity levels in materials used by the semiconductor industry ensure greater device functionality at smaller device geometries. The most commonly used solvent in the semiconductor fabrication process, ultra pure water (UPW), is not immune to meeting these increasingly stringent specifications. Committees for the International Technology Roadmap for Semiconductors (ITRS) set specifications for materials based on future semiconductor device geometry trends. The ITRS roadmap presently has specifications for critical metallic impurities in UPW set at less than 1 ppt. This specification will continue though the year 2007. However, changes for this specification will require no critical metallic impurity be greater than 0.5 ppt (500 ppq) starting in the 2008 and beyond. But, this leads to some very important questions: how can a cutting edge fab meet these specifications, and more importantly, what steps must be taken to accurately measure impurities at these low levels?

Initial investigations into quantitative method development for the analysis of metallic impurities at the sub-ppt level revealed that special care must be taken during sampling collection, sample transport, and sample analysis steps. Sample collection, while generally considered as simple and routine, must be carefully assessed in order to eliminate the introduction of elemental contaminants from the sampling environment, sampling technique, and maintain sample integrity through sample transport. Sample analysis, even though completed within a clean room laboratory environment, must also be carefully scrutinized. In this work, data is presented regarding the validation of new analytical methods that, not only satisfy the analysis requirements of the current ITRS guidelines, but will also meet the new analytical guidelines for 2008. Examples of how ppq analysis of UPW has been used to solve process problems in current semiconductor fabs are also demonstrated.

Introduction

Ultra pure water (UPW) is the most commonly used solvent in the semiconductor fabrication process. Historically, the technology for the purification of UPW has been adequate to maintain the purity levels needed for the semiconductor industry. While minor changes over the past decade have been made, the basic technology involved in the purification process has basically remained the same. Even analytical technologies have been inadequate to measure the true metallic impurity levels in semiconductor-grade UPW. However, decreases in line-width geometries of semiconductors have lead to new concerns about impurities in UPW. Committees for the International Technology Roadmap for Semiconductors (ITRS) set specifications for materials based on these future semiconductor device geometry trends **(1)**. The ITRS committee that sets specifications for UPW purity has determined that specifications must be changed to meet the requirements of the new line-width geometries of the next generation of semiconductors. Proposed metallic impurities guidelines from 2005 through 2013 are detailed in Table A. Current UPW purity specifications for semiconductor fabs require no metallic impurity should be greater than 1 part-per-trillion (ppt) for the following critical metals: Al, As, Ba, Ca, Co, Cu, Cr, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sn, Ti, and Zn. ITRS has agreed that these requirements will be adequate throughout the year 2007. However, these specifications change for 2008 and beyond to 0.5 ppt., or 500 parts-per-quadrillion (ppq).

Analytical methodologies have been developed for the analysis of UPW to current ITRS specifications **(2-4)**. However, the new 2008 guidelines represent a new challenge for the analytical field because they will call for the detection of impurities below the capability of most analytical methods. New analytical methods are needed to not only detect whether the new specifications can be met, but also provide a quantitative determination of metallic impurities for a system to determine whether the system truly meets the new specifications.

Experimental

The preparation of new sampling bottles required two steps: PFA sample bottles were leached with a mixture of 10% HNO_3 [Fisher Optima grade] / 10% HF [Stella SA-X grade, Japan] for two weeks, followed by

© 2006 Balazs Analytical Services
A division of Air Liquide Electronics U.S. LP

soaking in 10% HF for two weeks. Prior to sample acquisition, each sample bottle was rinsed with 5% HF [Stella SA-XX grade, Japan] followed by copious amounts of semiconductor grade UPW.

UPW samples were collected by allowing UPW from selected sampling points to flow directly into the specially cleaned sample bottles. Wafer fab UPW bath samples for fab troubleshooting purposes were collected using the PFA sampler shown in Figure 1. Following sample collection, the UPW samples were acidified with a semiconductor-grade acid and allowed to stand for at least 4 hrs. Aliquots of the collected sample were then transferred to pre-cleaned PFA evaporation bottles. The bottles were weighed and evaporated to dryness using an ultra-clean sample evaporation system. The patented, custom design evaporation system is constructed with all PFA parts and features a non-contact heat source (Figure 2) **(5)**. Residues were dissolved in a solution of 2% HNO_3/2% H_2O_2 [semiconductor grade] for final analysis. Existing methods for the determination of metallic impurities to current ITRS specifications required a preconcentration to bring the analyte concentration in the solution into the dynamic range of the analysis instrument. A constant total pre-concentration factor was used for all samples for further investigations. Elemental analyses were carried out on a PE-Sciex 6100 DRC 2 Dynamic Reaction Cell Inductively Coupled Plasma Mass Spectrometer (DRC ICP-MS) [PE-Sciex, Norwalk, CT, USA] equipped with a quartz spray chamber [PE-Sciex, Norwalk, CT, USA] and 50 µL/min PFA micronebulizer [Elemental Scientific, Omaha, NE.]. The Dynamic Reaction Cell uses post-plasma ion-molecule reactions to eliminate atomic and molecular isobaric interferences that are created within the plasma during analysis. The DRC ICP-MS instrument design has been described in detail by Tanner, Baranov, and Vollkopf **(6)**. Individual working standards were prepared by serial dilution from separate NIST-traceable spectroscopy standards [High Purity Standards, Charleston, SC]. Semiconductor-grade 18.2 MΩ deionized water was used throughout the experiments for dilutions.

Discussion

PPQ Sampling Contamination Considerations

While it is impossible to eliminate all potential contamination sources, one can take steps to minimize contamination effects. However, what can be seen is that virtually anything that comes in contact with the sample, whether solid, liquid, or gas, has the potential to influence the final analysis results. Over several years, analysis of many materials has been done to identify the highest purity materials possible for use in such difficult sample collection efforts.

As a rule of thumb, sampling is generally revered as routine, with only modest training needed to complete the task adequately. However, sampling at the ppq levels requires more detailed examination. One example of contamination potential is the sampling environment itself. Sampling in uncontrolled environments can lead to particulate matter dissolved into the sample by either falling into open sampling bottles, or by Venturi effects seen in the air flow around the UPW sampling stream. Static charge also plays a large part in contamination because particulate matter are especially attracted to the high-purity bottles made from copolymer materials that are prone to static buildup. One particle of iron oxide, for example, about 0.1 micron in size dissolved in one milliliter of water is equivalent to 2 femtogram per gram (fg/g) **(7)**. Because of this contamination risk, routine sampling collection procedures are inadequate for testing to ppq levels.

Another point of consideration once the sample has been collected is how the sample will be transported to the analysis location. Factors such a heat, pressure, light, surface-to-volume ratio, physical agitation, packaging material, and container positioning will all affect the final result. One must take steps to minimize contamination from these factors. Some of these factors can be minimized by shipping the sample bottles to and from the sampling site doubly bagged. The packaging material Vermiculite is never used due to the significant levels of contamination from the fine dust which makes up this material. Foam packing is generally used to keep samples from shifting. One also must consider if the person who transports the sample is knowledgeable about these factors. Samples can be compromised simply because the person shipping the samples was not aware such precautions were needed.

Additionally, contamination may be introduced even during the analysis process. During sample transfer steps for example, the bottles for the sampling and analysis can be contaminated if precautions are not taken. Even in an environment, such as a class 10 cleanroom, the possibility of contamination cannot be ruled out. Assuming an air flow of 90 linear feet per minute, ten CaO particles per cubic foot that are 0.5 µm in size could still be present in the air. If one transfers a 50 mL sample into a vessel with a 1½ inch opening for about two minutes to conduct sample transfer, two particles could enter the vessel yielding a possible contamination of 6 fg/g **(7)**. The threat of

© 2006 Balazs Analytical Services

contamination is still present even in this type of cleanroom environment. Therefore, every step in the sample analysis train, from sample collection to sample analysis and data interpretation has been keenly looked at and potential sources of contamination minimized.

Solving Problems in the Fab

The methods developed for measurement of UPW at current ITRS specification levels have been used to solve process problems in real fabs. With the use of these methods, problem areas inside fab processing units were identified. Two such examples are listed below.

Case #1: Two different UPW distribution systems were investigated for stainless steel contamination. Many components (pumps, UV sterilizers, etc.) are typically constructed with stainless steel parts that can lead to contamination in the UPW stream. Samples were collected from two different semiconductor fab areas. Additionally, the two different UPW distribution systems were sampled at several points [Table B]. This sampling strategy allowed for the accurate characterization of several wafer fab sites. UPW point-of-use samples were also taken using the PFA sampling device. This device makes use of all PFA material with no moving parts or o-rings. Simply compressing and releasing the sample bottle creates a vacuum that allows the transfer of sample into the pre-cleaned sample bottle. The only point of contact for the sample is PFA tubing and PFA sampling bottles. Two point-of-use UPW samples from distinct sources were compared [Table C]. The data clearly demonstrate differences in the UPW. These differences helped identify contamination sources at the point-of-use and throughout the distribution system.

Case#2: Hot and cold UPW supply systems leading to a wafer rinse bath tool were investigated for ppq-level impurities. TXRF analysis of process wafers done previously indicated a Cu source somewhere within the rinsing procedure. Further investigations into the source of the Cu contamination lead to the possibility that one of the UPW supplies could be suspect. However, analysis of the UPW baths showed Cu results below the detection limit of routine analytical procedures. Three samples were collected from the system, one from the cold supply and two from the hot supply. PPQ analysis results of the different samples collected are shown in Table D. Results clearly indicate a Cu contamination source coming from the first hot rinse supply. These results enabled the fab to locate a defective part within the UPW stream coming from the first UPW rinse supply.

Efforts to reach new 2008 ITRS Specifications

The work mentioned above demonstrates the ability our laboratories have to collect and analyze UPW samples to current ITRS specifications. However, the question now becomes whether these methods could be further expanded to analyze impurities in UPW to such an aggressive specification as to what is called for in 2008 and beyond. To answer this question, experiments were performed by preconcentration of eight different UPW samples collected from our own UPW system. The samples were spiked at the new 2008 specification level of 0.5 ppt (500 ppq) for each ITRS required element. A preconcentration factor of 60 was used for these experiments because the desired spike levels were a factor of two lower than previous validation work. The new detection limits calculated for this work indicated the spike levels would be significantly above detection levels. The DRC gas parameters used to eliminate isobaric interferences, and resulting calculated method detection limits are shown in Table E. Acceptable spike recoveries, from 84%-115%, were observed for all elements tested [Table F]. The data not only reflects the ability to detect impurities at the 2008 specifications, but also reflects the ability to reliably quantitate these impurities at such levels. These methods could allow a fab to completely determine if they are within compliance of the new ITRS specifications.

The ITRS committee is also currently considering expanding the critical metals list from the current 18 elements to a 30 element list currently used for analysis of other chemicals used in the semiconductor industry. Work has been done to test if this expanded list is feasible to meet. As seen in Table G, the extended list of metals is possible. Au, Pd, and Ru are elements also included in the proposed extended metals list. The feasibility studies for these elements will be tested in future experimental trials.

Conclusion

Analysis at the part-per-quadrillion level requires careful examination of the data to identify sources of contamination in both the sampling and analysis procedures. The methods described here have shown that detection and quantification at ppq levels are possible for the analysis of ultra clean UPW systems. We have

 © 2006 Balazs Analytical Services

demonstrated, with the use of our PFA sampling system, the ability to obtain clean samples from process baths. Ultra-clean sampling, sample preconcentration and DRC-ICP-MS analysis allow the ability to characterize and diagnose problem areas in UPW process streams at the ppq level.

Meeting the requirements for the new specifications of UPW purity beginning in 2008 will be challenging. Analysis of UPW samples to determine whether or not a system can meet these new specifications also represents special challenges. However, it has been shown that these analytical challenges can be met if the proper precautions in sampling and analysis are taken with regards to minimizing contamination sources. Data reveal the possibility of contamination can be significant in any step of the analysis process. Minute particles from the sampling environment, conditions present during sample transport, sampling containers, and even analytical environment and materials all can affect the final result. Investigations into the effects of these factors, and minimizing their contamination contributions, have lead to success in the analysis at the ppq levels.

References

1. ITRS Guidelines, 2005 Edition
2. Schoen, S.; Anderson, S.; Bollinger, D.; Haddix, M. "Two New Tests for UPW-Meeting the Challenge for New Technologies", *Proceedings of* the *25*th Annual Semiconductor Pure Water and Chemicals Conference (February, 2006)
3. Schleisman, A.J.; Bollinger, D; Tillotson, B.; Anderson, S. "Analytical Challenges at the fg/g Level in Ultrapure Water", *Proceeding of* the 18th Annual Semiconductor Pure Water and Chemicals Conference (March, 1999)
4. Bollinger, D; Anderson, S.; Schleisman, A.J. "Sampling and Analysis at the PPQ Levels: Considerations and Pitfalls", *Proceedings of* Pittsburg Conference 2001 (March, 2001)
5. Bollinger, D; Schleisman A.J. "Preparation and Analysis of High Purity Semiconductor Chemicals by Graphite Furnace Atomic Absorption at the Part-Per-Trillion Level", *Proceedings of 1994* FACSS Conference, (October 1994)
6. Tanner, S.; Baranov, V.; Vollkopf, U. *Plasma Source Mass Spectrometry: New Developments and Applications*, pp. 34-63, The Royal Society of Chemistry, Cambridge, UK. (1999)
7. Schleisman, A.J.; Bollinger, D.; Tillotson, B.; Anderson, S. "Method Validation of Ca, Na, K, and Fe at the fg/mL Level in Semiconductor-Grade Chemicals", *Proceedings of* 1998 FACSS Conference (October, 1998)
8. Pennington, B., Air Liquide-Balazs, personal correspondence (September, 2006)

 © 2006 Balazs Analytical Services

Tables and Figures

DI H2O Critical Metals	2005	2006	2007	2008	2009	2010	2011	2012	2013
PPT (each)	**<1**	**<1.0**	**<1.0**	***<0.5***	***<0.5***	***<0.5***	***<0.5***	***<0.5***	***<0.5***

Table A: ITRS guidelines for metallic impurities in UPW through the year 2013. The specification changes from 1 ppt to 0.5 ppt in 2008.

Figure 1: Ultrapure PFA Sampler. The sampler uses no o-rings or moving parts allowing for ultra-clean sample collection.

© 2006 Balazs Analytical Services

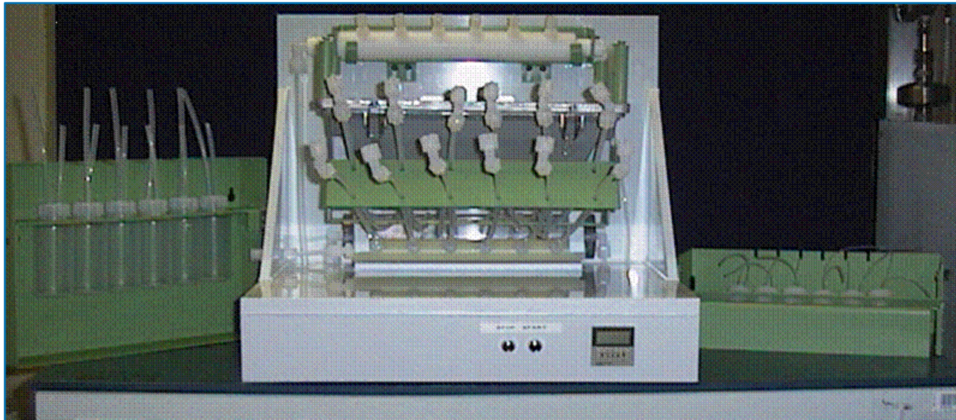

Figure 2: Sample evaporation system. This patented system uses only ultra-high purity PFA parts, contains no o-rings, and utilizes a non-contact heat source that evaporates and preconcentrates chemical samples.

Fab I

Sample	Ca	Ti	Cr	Fe	Ni	Cu	Zn
Post-polish*	< 0.85	< 0.15	< 0.25	< 0.50	< 0.15	< 1.00	< 1.00
	< 0.85	< 0.15	< 0.25	< 0.50	< 0.15	< 1.00	< 1.00
Pre-UV**	2.35	< 0.15	< 0.25	0.91	< 0.15	< 1.00	< 1.00
	2.56	< 0.15	< 0.25	0.73	< 0.15	< 1.00	< 1.00

Fab II

Sample	Ca	Ti	Cr	Fe	Ni	Cu	Zn
Post-polish	8.61	< 0.15	1.30	0.94	5.57	< 1.00	< 1.00
	9.78	< 0.15	1.26	0.97	5.38	< 1.00	< 1.00
Pre-UV	38.65	0.38	1.38	7.72	4.45	< 1.00	3.13
	39.74	0.35	1.47	7.25	4.49	< 1.00	3.30

* Post polish – After ion exchange beds

** Pre-UV – Before ultraviolet sterilizers

Table B: PPQ characterization analysis results of two separate UPW distribution systems. All results are in ppt. Distinct differences in the two systems can be seen.

Element	Point-of-Use I (ppt)	Point-of-Use II (ppt)
Ca	< 0.85	< 0.85
	< 0.85	< 0.85
Ti	< 0.15	1.31
	< 0.15	1.19
Cr	1.07	1.25
	1.04	1.15
Fe	0.74	< 0.50
	0.66	< 0.50
Ni	8.49	0.73
	8.14	0.47
Cu	2.68	2.69
	2.46	2.62
Zn	< 1.00	2.08
	< 1.00	2.10

Table C: PPQ analysis results of two different point-of-use sources. Differences between the two sources can be compared. All results are in ppt.

SAMPLE	Cu
Rinse Bath COLD DI H_2O Supply	< 0.17
	< 0.17
1st Rinse Bath HOT DI H_2O Supply	4.74
	4.92
2nd Rinse Bath HOT DI H_2O Supply	< 0.17
	< 0.17

Table D: PPQ analysis of hot and cold UPW supplies for Cu. All results are in ppt. The results clearly show the system containing the Cu contamination source.

© 2006 Balazs Analytical Services

ELEMENT	INTERFERING SPECIES	Method Detection Limit (ppt) (3 sigma)
^{7}Li	---	0.11
^{23}Na	---	0.11
^{24}Mg	$^{12}C-^{12}C^{+}$	0.15
^{27}Al	$^{11}B-^{16}O^{+}$, $^{12}C-^{14}N^{+}$, $^{28}Si^{+}$	0.17
^{39}K	$^{38}Ar-^{1}H^{+}$	0.24
^{40}Ca	$^{40}Ar^{+}$	0.18
^{48}Ti	$^{36}Ar-^{12}C^{+}$, $^{14}N-^{16}O-^{18}O^{+}$	0.09
^{52}Cr	$^{40}Ar-^{12}C^{+}$, $^{38}Ar-^{14}N^{+}$	0.14
^{55}Mn	$^{40}Ar-^{15}N^{+}$, $^{40}Ar-^{14}N-^{1}H^{+}$	0.04
^{56}Fe	$^{40}Ar-^{16}O^{+}$, $^{41}Ar-^{14}N-^{1}H^{+}$	0.05
^{59}Co	$^{40}Ar-^{19}F^{+}$, $^{40}Ar-^{18}O-^{1}H^{+}$	0.13
^{58}Ni	$^{40}Ar-^{18}O^{+}$, $^{40}Ar-^{17}O-^{1}H^{+}$	0.12
^{63}Cu	$^{31}P-^{16}O-^{16}O^{+}$	0.13
^{64}Zn	$^{36}Ar-^{28}Si^{+}$, $^{128}Xe^{++}$	0.15
^{75}As	$^{40}Ar-^{35}Cl^{+}$, $^{40}Ar-^{19}F-^{16}O^{+}$	0.13
^{120}Sn	---	0.12
^{138}Ba	---	0.08
^{208}Pb	---	0.11

Table E: DRC gas parameters and new calculated detection limits for 2008 ITRS specifications.

© 2006 Balazs Analytical Services

Element	Method Blanks			0.5 ppt Method Spikes								Average	Coefficient
	Blk #1	Blk #2	Average	#1	#2	#3	#4	#5	#6	#7	#8	% Recovery	of Variation
Li	0.01	0.02	0.02	0.49	0.55	0.56	0.53	0.60	0.56	0.50	0.55	106%	7.0%
Na	0.45	0.41	0.43	0.95	1.01	0.99	0.90	0.95	0.99	0.99	0.94	107%	4.0%
Mg	0.04	0.04	0.04	0.69	0.54	0.61	0.66	0.55	0.63	0.62	0.59	114%	8.0%
Al	0.03	0.04	0.04	0.67	0.57	0.61	0.67	0.53	0.59	0.68	0.56	115%	9.0%
K	0.02	0.09	0.06	0.51	0.49	0.55	0.71	0.56	0.51	0.57	0.67	103%	14.0%
Ca	0.12	0.11	0.12	0.64	0.61	0.64	0.60	0.60	0.66	0.78	0.70	108%	9.0%
Ti	0.20	0.02	0.11	0.51	0.51	0.54	0.56	0.54	0.48	0.52	0.57	84%	6.0%
Cr	0.02	0.01	0.02	0.47	0.50	0.44	0.55	0.52	0.43	0.56	0.52	97%	10.0%
Mn	0.00	0.01	0.01	0.56	0.55	0.56	0.53	0.55	0.53	0.53	0.55	108%	2.0%
Fe	0.04	0.01	0.03	0.53	0.54	0.55	0.55	0.57	0.56	0.58	0.54	106%	3.0%
Co	0.00	0.01	0.01	0.61	0.54	0.55	0.56	0.48	0.48	0.51	0.50	105%	8.0%
Ni	0.06	-0.01	0.03	0.53	0.49	0.56	0.58	0.49	0.58	0.59	0.58	105%	8.0%
Cu	-0.01	-0.01	-0.01	0.51	0.53	0.50	0.55	0.56	0.50	0.52	0.42	104%	8.0%
Zn	0.03	0.01	0.02	0.52	0.55	0.63	0.56	0.63	0.49	0.56	0.61	110%	9.0%
As	0.05	0.03	0.04	0.50	0.42	0.46	0.49	0.46	0.53	0.40	0.46	85%	9.0%
Sn	0.02	0.00	0.01	0.53	0.45	0.53	0.54	0.53	0.45	0.53	0.55	101%	8.0%
Ba	0.01	0.01	0.01	0.53	0.52	0.54	0.56	0.55	0.47	0.53	0.53	104%	5.0%
Pb	0.02	0.01	0.02	0.51	0.55	0.54	0.55	0.47	0.58	0.58	0.54	104%	7.0%

Table F: 0.5ppt (500 ppq) spike recoveries for the proposed ITRS 2008 metals list. The data was collected using eight separate UPW samples.

Element	Method Blanks			0.5 ppt Method Spikes								Average	Det. Lim.
	Blk #1	Blk #2	Average	#1	#2	#3	#4	#5	#6	#7	#8	% Recovery	(3-sigma)
Be	0.08	0.03	0.06	0.51	0.51	0.59	0.62	0.50	0.59	0.55	0.47	98%	0.16
V	0.02	0.02	0.02	0.46	0.51	0.49	0.52	0.50	0.37	0.43	0.47	90%	0.15
Ga	0.00	0.00	0.00	0.49	0.49	0.52	0.53	0.51	0.41	0.49	0.52	99%	0.11
Ge	0.00	0.00	0.00	0.45	0.52	0.51	0.51	0.50	0.47	0.50	0.48	99%	0.07
Sr	0.00	0.00	0.00	0.51	0.51	0.51	0.52	0.50	0.50	0.52	0.51	102%	0.02
Zr	0.00	0.00	0.00	0.50	0.53	0.49	0.54	0.49	0.51	0.52	0.52	103%	0.05
Nb	0.00	0.00	0.00	0.47	0.51	0.50	0.52	0.50	0.48	0.49	0.49	99%	0.05
Mo	0.00	0.00	0.00	0.51	0.54	0.54	0.56	0.50	0.53	0.50	0.55	106%	0.07
Ag	0.01	0.01	0.01	0.56	0.40	0.46	0.51	0.55	0.49	0.48	0.42	95%	0.17
Cd	0.00	0.00	0.00	0.49	0.47	0.50	0.47	0.54	0.57	0.52	0.55	103%	0.11
In	0.00	0.00	0.00	0.48	0.48	0.48	0.50	0.50	0.49	0.49	0.50	98%	0.03
Sb	0.00	0.00	0.00	0.47	0.48	0.50	0.57	0.59	0.50	0.56	0.51	105%	0.13
La	0.00	0.00	0.00	0.50	0.49	0.50	0.52	0.52	0.48	0.49	0.45	99%	0.07
Ta	0.00	0.00	0.00	0.45	0.41	0.49	0.52	0.50	0.40	0.48	0.49	94%	0.13
W	0.00	0.00	0.00	0.51	0.49	0.51	0.51	0.55	0.33	0.56	0.54	100%	0.22
Pt	0.00	0.00	0.00	0.51	0.57	0.57	0.58	0.53	0.47	0.43	0.44	103%	0.18
Tl	0.00	0.00	0.00	0.46	0.51	0.50	0.51	0.54	0.51	0.46	0.47	99%	0.09
Bi	0.00	0.00	0	0.49	0.49	0.52	0.49	0.52	0.45	0.52	0.53	100%	0.08

Table G: 0.5 ppt (500 ppq) spike recoveries and calculated method detection limits for the proposed ITRS 2008 extended metals list.

© 2006 Balazs Analytical Services