Direct Analysis of Trace Metallic Impurities in High Purity Hydrochloric Acid by 7700s/7900 ICP-MS

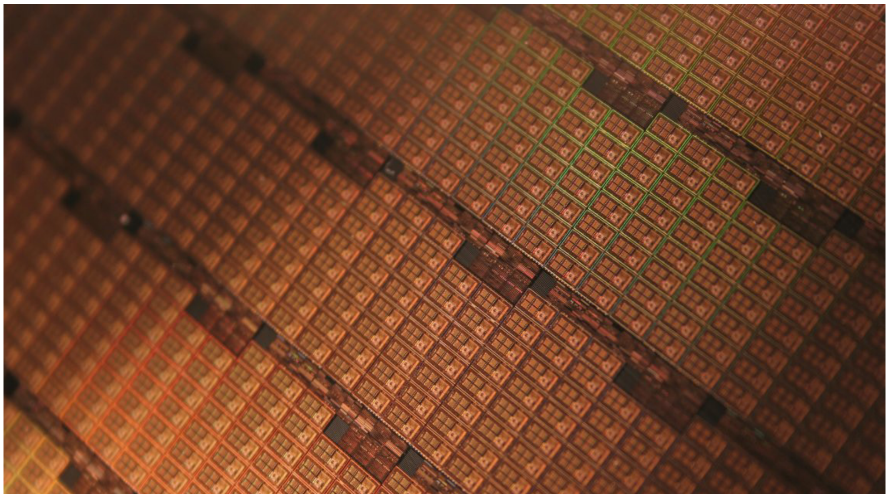
Application note

Semiconductor analysis

Author

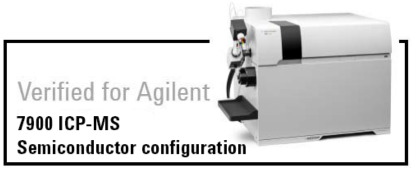
Junichi Takahashi

Agilent Technologies
Tokyo, Japan



Abstract

This application note illustrates the advanced analytical performance and robustness of the Agilent 7700s/7900 ICP-MS for the direct determination of metallic impurities in high purity concentrated hydrochloric acid (HCl). The 7700s/7900 incorporates an Octopole Reaction System (ORS), which effectively removes polyatomic interferences, allowing ultimate detection limits to be achieved for elements that suffer from severe chloride-based interferences. For example, the polyatomic ion $^{40}Ar^{35}Cl^+$ can be eliminated by the ORS allowing the direct measurement of As at mass 75, and permitting accurate analysis of As at trace levels in undiluted concentrated HCl. Enabling direct analysis of concentrated acids eliminates the dilution step from the sample preparation procedure, and so significantly reduces the potential for sample contamination.



Agilent Technologies

Introduction

Hydrochloric acid is frequently used to remove metallic impurities on the surface of silicon wafers. Together with hydrogen peroxide, this cleaning method is well known as RCA Standard Clean 2 (SC-2). The manufacturing process of semiconductor devices requires routine monitoring of contaminants in HCl, and ICP-MS is the accepted tool for this purpose. Although HCl is diluted prior to use for SC-2, the concentration of industrial grade HCl is usually 20% or 35%, depending on the method of production. Because HCl is highly corrosive; direct introduction of concentrated HCl into an ICP-MS is normally avoided. Moreover, introduction of HCl at high concentration leads to the formation of a large number of polyatomic ions in the ICP, which cause significant spectral interferences with some key elements of interest, for example, $H_2{}^{37}Cl^+$ on $^{39}K^+$, $^{35}Cl^{16}O^+$ on $^{51}V^+$, $^{35}Cl^{16}OH^+$ on $^{52}Cr^+$, $^{35}Cl^{37}Cl^+$ on $^{72}Ge^+$, $^{37}Cl_2{}^+$ on $^{74}Ge^+$, and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Consequently, some methodology for the analysis of high purity HCl by ICP-MS has recommended sample pre-treatment steps to remove the chloride matrix, which can lead to analyte loss and sample contamination. However, the Agilent 7700s/7900 ICP-MS is manufactured using robust and anti-corrosive materials, which means that undiluted HCl can be analyzed directly, while the ORS drastically improves the efficiency of removing polyatomic ions, allowing many elements to be determined at lower detection limits than were previously possible.

Experimental

Instrumentation

An Agilent 7700s ICP-MS fitted with an optional third cell gas mass flow controller (in addition to the standard collision (helium) and reaction (hydrogen) gas lines) was used throughout. The optional cell gas line is required for specialized applications, including analyses where optimum interference removal requires a highly reactive cell gas such as ammonia. The standard 7700s ICP-MS sample introduction system was used, consisting of a platinum sampling cone, platinum skimmer cone, PFA nebulizer, and quartz torch.

Materials and reagents

High purity hydrochloric acid, TAMAPURE-AA100 (20%), was purchased from TAMA Chemicals, Japan. Undiluted HCl was introduced directly into the ICP-MS, to eliminate any sample preparation steps and thereby significantly reduce the potential for sample contamination.

Calibration standard solutions were prepared by spiking a mixed multielement standard (SPEX Certiprep) into an acid blank at 10, 20, 50 and 100 ppt.

Results and Discussion

Detection limits and background equivalent concentrations

Forty two elements were measured using the Agilent 7700s ICP-MS operating in multiple tune modes. Data was acquired in an automated sequence of cool plasma, no gas and gas modes, during a single visit to the sample vial. The sample-to-sample run time was approximately 6 minutes. Data for each of the modes was combined automatically into a single report for each sample. Detection Limits (DLs) and Background Equivalent Concentrations (BECs) are show in Table 1. DLs were calculated from 3σ of 10 measurements of the acid blank.

Table 1. Agilent 7700s ICP-MS DLs and BECs in 20% high purity HCl.

Element	*m/z*	Mode	DL (ppt)	BEC (ppt)
Li	7	Cool	0.016	0.004
Be	9	No gas	0.13	0.11
B	11	No gas	4.5	9.7
Na	23	Cool	0.44	1.3
Mg	24	Cool	0.11	0.22
Al	27	Cool	0.79	1.1
K	39	Cool/NH_3	0.40	0.50
Ca	40	Cool/NH_3	1.1	2
Ti	48	He	0.71	0.68
V	51	NH_3	2.1	2.0
Cr	52	Cool/He	4.5	12
Mn	55	He	1.57	2.84
Fe	56	Cool	2.4	4.2
Co	59	He	0.20	0.13
Ni	60	He	3.03	4.43
Cu	63	Cool	0.49	0.59
Zn	64	He	2.1	2.9
Ga	71	He	0.47	0.31
Ge	74	He	2.1	13
As	75	He	4.0	16
Se	78	He	5	5.5
Sr	88	He	0.21	0.061
Zr	90	He	0.11	0.03
Nb	93	He	0.34	0.43
Mo	98	He	0.52	0.67
Ru	101	He	0.05	0.01
Pd	105	He	0.57	0.51
Ag	107	He	0.056	0.033
Cd	114	He	0.41	0.52
Sb	121	He	2	2.8
Te	125	He	5.4	1.1
Ba	138	He	0.076	0.067
Hf	178	He	0.06	0.015
W	182	He	0.094	0.13
Re	185	He	0.49	0.54
Ir	193	He	0.1	0.07
Au	197	He	0.15	0.4
Tl	205	He	0.054	0.024
Pb	208	He	0.37	0.56
Bi	209	He	0.44	0.33
Th	232	He	0.01	0.003
U	238	He	0.032	0.013

Cr and K determination

Cool plasma is a proven technique used to remove plasma-based interferences. Although it has been largely superseded by Collision Reaction Cell (CRC) methodology, cool plasma remains the most effective analytical mode for some elements in certain matrices. Furthermore, the Agilent 7700s/7900 ICP-MS provides an enhanced cool plasma mode of operation, delivering improved robustness and stability due to the use of the new frequency matching RF generator. Used together with the ORS, cool plasma has recently been demonstrated to provide a new, powerful mode to remove interferences [1].

Because the major isotope of chromium ($^{52}Cr^+$) suffers an interference from $^{35}Cl^{16}O^1H^+$, chromium was determined using cool plasma and He mode. With cool plasma (low plasma RF power), production of $ClOH^+$ ions is suppressed because of its high ionization potential (I.P.) of 11 eV [2]. For further analytical improvement, He mode was used in combination with the cool plasma conditions to completely eliminate any remaining $^{35}Cl^{16}OH^+$ ions. The resultant calibration curve for ^{52}Cr is shown in Figure 1.

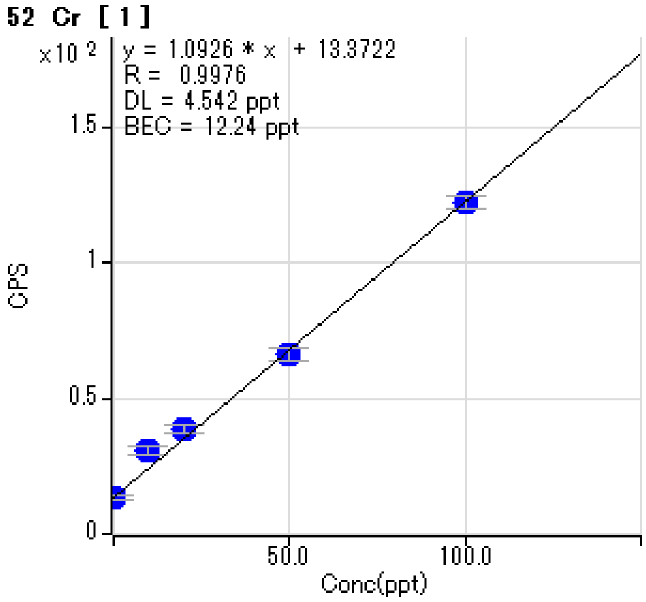


Figure 1. ^{52}Cr calibration curve obtained using He mode and cool plasma.

The approach of using the ORS with cool plasma is also effective for other elements such as potassium. In order to suppress the interference of $H_2{}^{37}Cl^+$ on $^{39}K^+$, ammonia was selected as the cell gas with cool plasma. While there are very few cases where such highly reactive cell gases are required, there are some specific cases where such gases offer the lowest DLs. The intense $H_2{}^{37}Cl^+$ interference that affects K at mass 39 is not very reactive with H_2, so H_2 cell mode does not give sufficiently good interference removal for the lowest DL to be achieved in the highest purity HCl. The calibration curve for K (shown in Figure 2) illustrates the effective removal of the $H_2{}^{37}Cl^+$ interference using this novel mode of acquisition, providing a K BEC of 0.5 ppt and DL of 0.4 ppt in undiluted (20%) HCl.

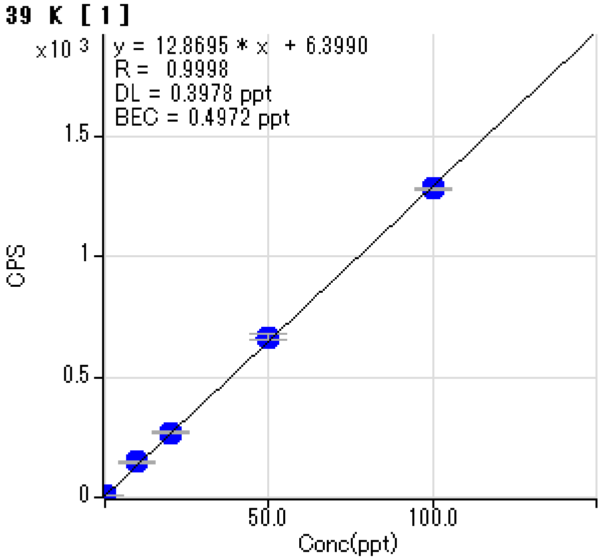


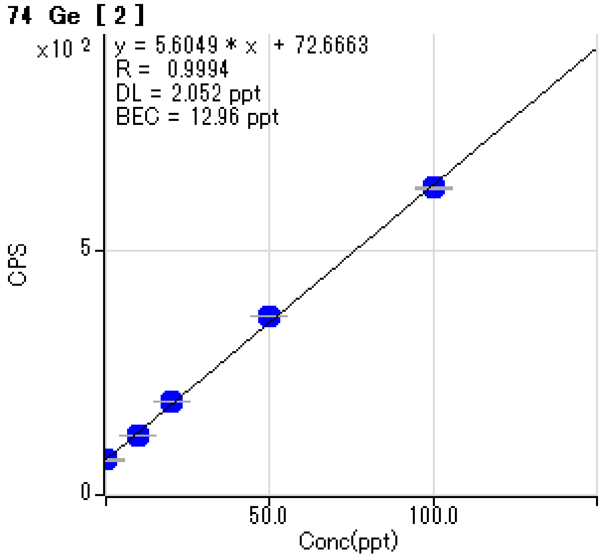
Figure 2. ^{39}K calibration curve obtained using NH_3 mode and cool plasma.

Ge and As determination

The ORS of the Agilent 7700s/7900 ICP-MS improves the removal of polyatomic interferences using He mode with Kinetic Energy Discrimination (KED), and also promotes Collision Induced Dissociation (CID) for relatively weakly bound polyatomic ions.

Germanium has 3 major isotopes at 70, 72 and 74 u that suffer from Cl-based polyatomic interferences, namely $^{35}Cl^{35}Cl^+$, $^{35}Cl^{37}Cl^+$ and $^{37}Cl^{37}Cl^+$. As the dissociation energy of Cl_2^+ is approximately 4 eV (3.95 eV for $^{35}Cl^{35}Cl^+$)[3], CID of Cl_2^+ would be unlikely to happen with the previous generation ORS, which provided a collision energy of only 0.9 eV in He mode. In contrast, in the later generation ORS the collision energy is increased to 5 eV, facilitating CID of several polyatomic ions including Cl_2^+. The performance of the 7700s with the ORS operating in high energy He mode is illustrated in Figure 3, which shows the calibration curve, DL and BEC for ^{74}Ge in a matrix of 20% HCl.

Figure 3. ^{74}Ge calibration curve obtained using high energy He mode.



Arsenic has a single isotope at *m/z* 75, that can suffer an interference from the polyatomic ion $^{40}Ar^{35}Cl^+$ that readily forms in a chloride matrix, making it extremely difficult to determine ^{75}As at low levels directly at mass 75. The ArCl interference on As can be avoided by indirectly measuring As at 91 u as the AsO^+ ion, which is formed either by applying cool plasma conditions or via the use of O_2 cell gas in the CRC. The latter approach utilizes hot plasma conditions but the measurement of As at mass 91 can still be affected by a $CaClO^+$ interference that forms from $CaCl^+$ when O_2 cell gas is used. Furthermore, AsO^+ at mass 91 suffers an isobaric interference from $^{91}Zr^+$, an overlap that does not occur under cool plasma conditions, since Zr is not ionized in a cool plasma. However, as with Cl_2^+, the higher collision energy of He mode in the ORS of the 7700s/7900 means that the $ArCl^+$ ion can also be dissociated by CID. This allows As to be determined at low levels directly at 75 u in 20% HCl, thus avoiding the use of both cool plasma and O_2 cell gas. A typical calibration curve for As in 20% HCl is shown in Figure 4.

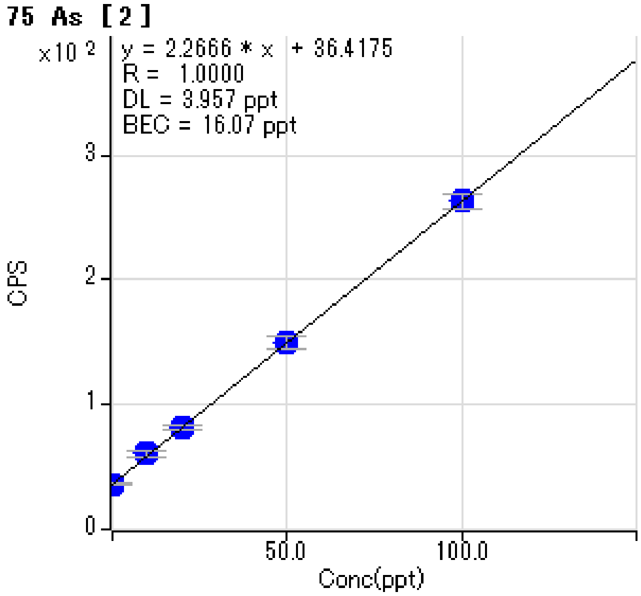


Figure 4. ^{75}As calibration curve obtained using high energy He mode.

V determination

The $^{35}Cl^{16}O^+$ interference on $^{51}V^+$ can also be eliminated using NH_3 as the cell gas, but under normal hot plasma conditions (1600 W). The increased collision energy of the ORS improves the reaction efficiency and gives a significant improvement in the DL and BEC, as shown in Figure 5.

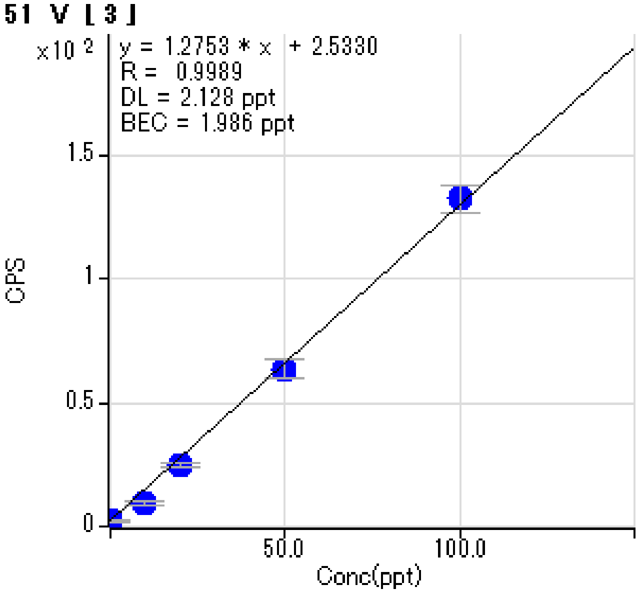


Figure 5. ^{51}V calibration curve obtained using NH_3 and normal plasma mode.

Conclusions

Agilent ICP-MS systems have been used for the analysis of trace metallic impurities in concentrated HCl for many years. Now, the Agilent 7700s/7900 ICP-MS with unparalleled cool plasma performance and ORS collision/reaction cell further improves the detection limits for the analysis of high purity acids. The ORS can be fitted with up to 3 cell gas lines (2 are included as standard), allowing total flexibility in both collision and reaction modes. The ORS cell improves performance for several critical elements by increasing the efficiency of both collision and reaction mode, and providing enhanced dissociation of certain polyatomic ions by CID. These developments now allow several elements like Cr, K, Ge, As and V to be determined at lower concentrations than previously possible in a chloride matrix.

References

1. Takahashi J.; Mizobuchi K. *Use of Collision Reaction Cell under Cool Plasma Conditions in ICP-MS*, Asia Pacific Winter Conference on Plasma Spectroscopy, 2008

2. Colbourne, D., Frost, D.C., McDowell, C.A., Westwood, N.P.C., *J. Chem. Phys.*, **1978**, 68, 3574.

3. Huber, K. P. and Herzberg, G., *Constants of Diatomic Molecules*, Van Nostrand Reinhold Co., 1979.

Verified for Agilent

7900 ICP-MS
Semiconductor configuration

www.agilent.com/chem

Published October 2, 2017
Publication number: 5990-7354EN

Agilent Technologies