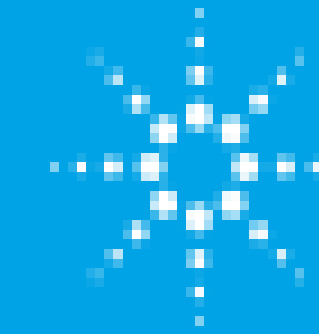# Determination of ultra-trace level impurities in high-purity metal samples by ICP-QQQ

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This paper describes ppt level impurity analysis of 49 elements in 0.1% high purity copper sample using simple one tuning mode on ICP-QQQ.

Introduction

Metals such as Cu, Al, Ta, W and Hf are used in semiconductor devices. Very high purity metals are required to ensure high performance and high production-yield of the devices. **ICP-MS** is used for the quality-control of these metal materials; but the application is not easy due to the requirement for ultra-low level impurity measurement in the relatively high-matrix metal sample digests.

A particular challenge is the ultra-trace measurement of alkali metal elements in the presence of the high matrix. Cool plasma is accepted in the semiconductor industry as a reliable technique to remove argon-based interferences such as Ar^+ and ArO^+ to enable low-level analysis of ^{40}Ca and ^{56}Fe. It can also be applied to the analysis of the alkali metal elements, providing lower background equivalent concentrations (BECs) than hot plasma conditions. This is because the low temperature plasma prevents the reionization of traces of the easily-ionized elements (EIEs) on the cones and ion lens. However, the cooler plasma also has poorer matrix tolerance, so is not suitable for the analysis of high matrix metals samples.

We report a new approach to the measurement of ultra-trace impurities in 0.1% high purity copper, using ICP-QQQ. The method uses **a new design of ion lens** that addresses the requirements of high matrix tolerance and ultra-low level measurement of the alkali metal elements. The new lens named "**m-lens**", which is optional on the Agilent 8900 ICP-QQQ, has a unique geometry which minimizes background signals from EIEs on the skimmer cone.

Experimental

Sample preparation

All samples and standards were prepared in 5% nitric acid (HNO_3) using semiconductor grade HNO_3, TAMAPURE AA-100 (TAMA CHEMICALS CO. Ltd, Kanagawa, JAPAN).

A 0.1% copper (Cu) sample was prepared as follows. A piece of 9N high purity copper was cleaned in diluted HNO_3, rinsed by ultra pure water (UPW), weighted (about 0.05g) and was dissolved in 5ml of 50% HNO_3 (UPW : HNO_3 = 50:50) and the solution was brought up with UPW to be 50ml .

Calibrations for 49 elements were prepared from multi element standards of xstc 331, xstc7 and xstc8, which were purchased from SPEX CertiPrep (NJ, USA) and used with appropriate dilution.

Experimental setup

Agilent 8900 #200 ICP-QQQ was used with the m-lens and the Ni base Pt skimmer cone. A PFA nebulizer was used in self aspiration with the standard sample introduction system.

Tuning and Method

Internal standard (ISTD) method was applied to correct matrix suppression and signal drift . All samples and standards were spiked with the three ISTD elements; Be, Sc and In to be 5.0, 0.5 and 0.5 ppb respectively.

Hot plasma conditions giving 1% CeO+/Ce+ ratio were used with **single cell tuning mode** which uses Oxygen(O_2) and Hydrogen(H_2) at the same time. Due to the MSMS reaction cell capability, the cell gas mixture successfully removed all interferences without the creation of new interference by product ions. The 49 elements were measured using the single tune mode summarized in Table1. Table 2 gives other details.

Table 1 : Tuning condition

Tuning Parameters	unit	value
RF power	W	1550
Carrier gas flow rate	L/min	0.70
Makeup gas flow rate	L/min	0.46
Sampling depth	mm	8.0
Extract 1	V	0.0
Extract 2	V	-70
Omega	V	+8
Omega Bias	V	-60
Cell gas and flow rate	ml/min	O2 = 0.2 and H2 = 7.0
Octopole Bias	V	-10
KED	V	-10
Axial Acceleration	V	+2.0

Table 2 : Interference and Data Acquisition parameters of 49 elements

| Element	Q1/Q2	interference	Reaction cell method	Detected ion	Integration time (s)	ISTD
Li	7/7		on-mass	Li+	0.5	Be
B	11/11		on-mass	B+	2.0	Be
Na	23/23		on-mass	Na+	0.5	Sc
Mg	24/24		on-mass	Mg+	0.5	Sc
Al	27/27	C2H3+	on-mass	Al+	0.3	Sc
Si	28/28	N2, CO+	on-mass	Si+	0.5	Be
P	31/47	NOH+, Cu++	mass shift	PO+	2.0	Be
S	32/48	O2+, Cu++	mass shift	SO+	2.0	Be
K	39/39	ArH+	on-mass	K+	0.5	Sc
Ca	40/40	Ar+	on-mass	Ca+	0.3	Sc
Ti	48/48	SO+	on-mass	Ti+	0.5	Sc
V	51/51	(ClO+)	on-mass	V+	0.3	Sc
Cr	52/52	ArC+,	on-mass	Cr+	0.3	Sc
Mn	55/55	ArNH+	on-mass	Mn+	0.3	Sc
Fe	56/56	ArO+	on-mass	Fe+	0.3	Sc
Co	59/59		on-mass	Co+	0.3	Sc
Ni	60/60		on-mass	Ni+	0.5	Sc
Zn	68/68	ArNN+, CuHHH+	on-mass	Zn+	2.0	Sc
Ga	71/71		on-mass	Ga+	0.5	In
Ge	72/72	ArAr+	on-mass	Ge+	0.5	In
As	75/91	(ArCl+)	mass shift	AsO+	1.0	In
Se	78/78	ArAr+	on-mass	Se+	3.0	In
Rb	85/85		on-mass	Rb+	0.3	In
Sr	88/88		on-mass	Sr+	0.5	In
Zr	90/106		mass shift	ZrO+	0.5	In
Nb	93/125	CuNO+	mass shift	NbO+	0.3	In
Mo	95/127	CuOO+	mass shift	MoOO+	0.5	In
Ru	99/99	ArCu+	on-mass	Ru+	0.5	In
Rh	103/103	ArCu+	on-mass	Rh+	0.3	In
Pd	105/105	ArCu+	on-mass	Pd+	0.5	In
Ag	107/107		on-mass	Ag+	0.3	In
Cd	111/111		on-mass	Cd+	1.0	In
Sn	118/118		on-mass	Sn+	0.5	In
Sb	121/121		on-mass	Sb+	0.5	In
Te	125/125		on-mass	Te+	3.0	In
Cs	133/133		on-mass	Cs+	0.5	In
Ba	137/137		on-mass	Ba+	0.5	In
Hf	178/194		mass shift	HfO+	0.5	In
Ta	181/213		mass shift	TaO+	0.5	In
W	182/214		mass shift	WOO+	0.5	In
Re	185/185		on-mass	Re+	0.5	In
Ir	193/193		on-mass	Ir+	0.5	In
Pt	195/195		on-mass	Pt+	0.5	In
Au	197/197		on-mass	Au+	0.5	In
Tl	205/205		on-mass	Tl+	0.3	In
Pb	208/208		on-mass	Pb+	0.3	In
Bi	209/209		on-mass	Bi+	0.3	In
Th	232/248		mass shift	ThO+	0.3	In
U	238/270		mass shift	UOO+	0.3	In

Results and Discussion

Calibration curves
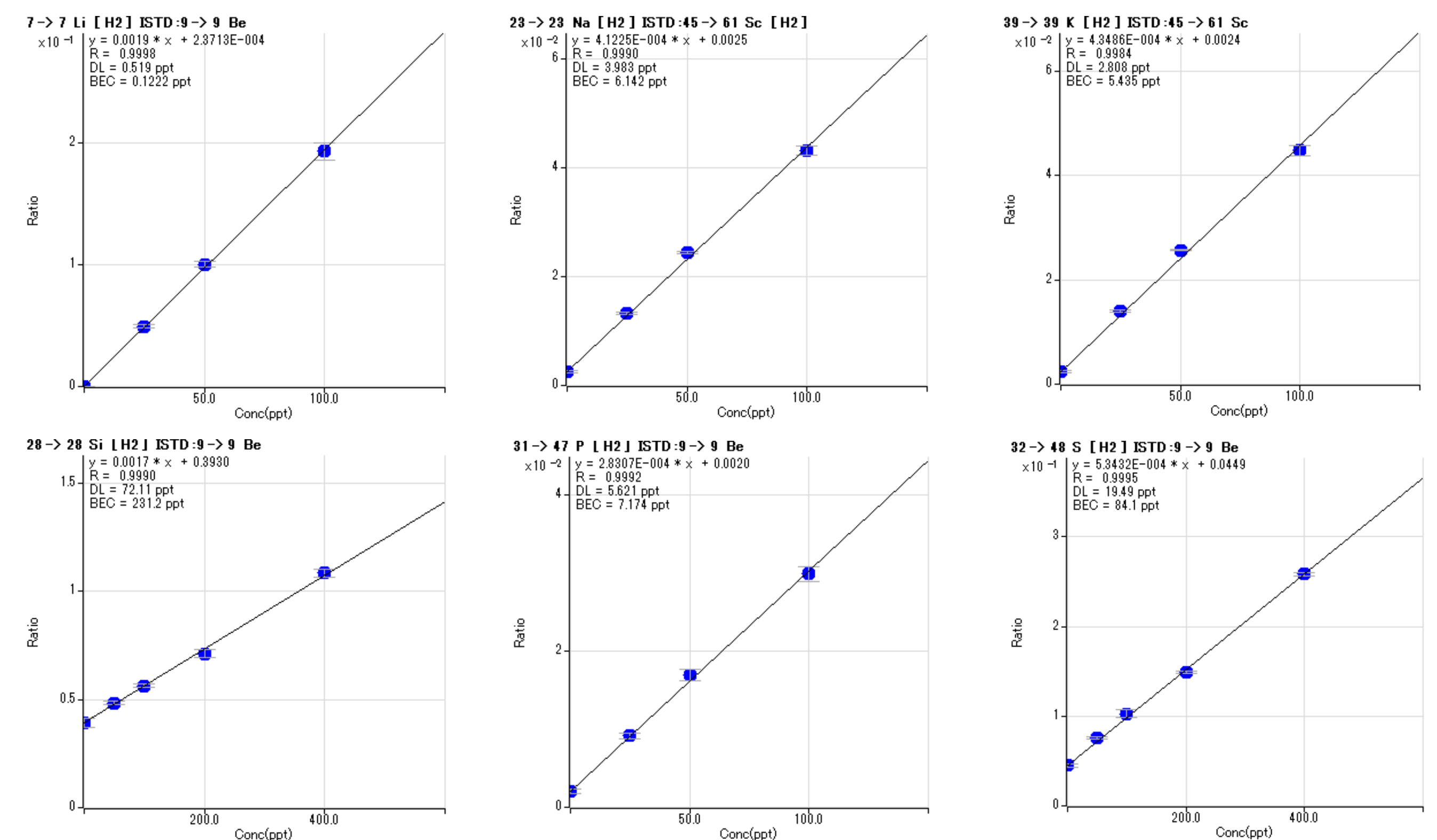
Figure 1 : Calibration curves of alkali metal elements and three challenging elements for ICP-MS.

Results and Discussion

BEC determined concentrated in 0.1% Cu sample, spike recovery test and stability test
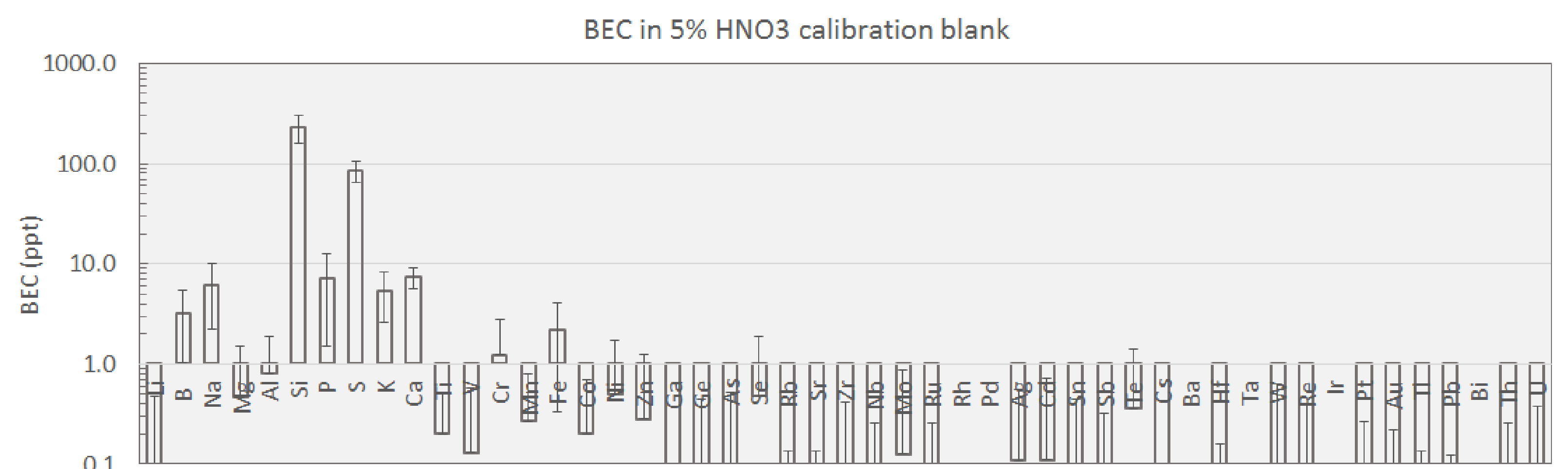

Figure 2 BEC in 5% HNO3 blank (Error bar = 3σ D.L.): Parts per trillion (ppt) level BEC was achieved for alkali elements; Li, Na and K with the hot plasma conditions used. **Note that** additionally, 100s ppt BEC was achieved for the most challenging elements; S (84ppt) and Si (231ppt) due to MSMS reaction cell capacity .
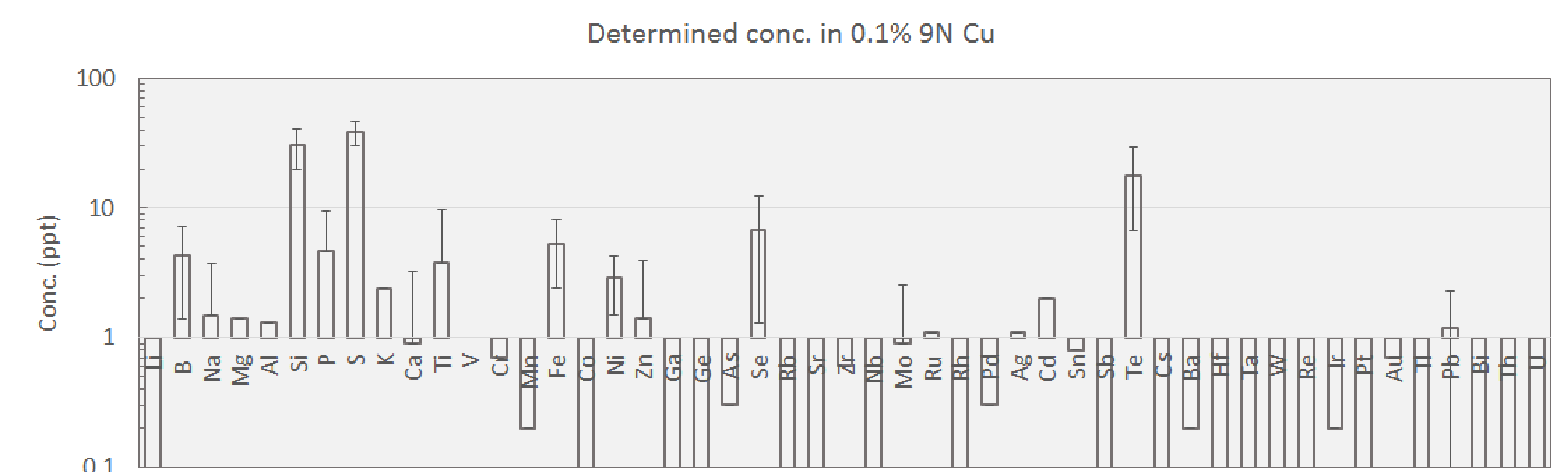

Figure 3 Determined conc. in 0.1% 9N Cu sample (Error bar = variation in three samples): Except Si, S and Te, conc. < 10ppt was obtained. The O_2+H_2 reaction cell removed significant spectral interferences from $ArCu^+$ on Ru, Rh and Pd , allowing the determination of those elements at ultra low levels.
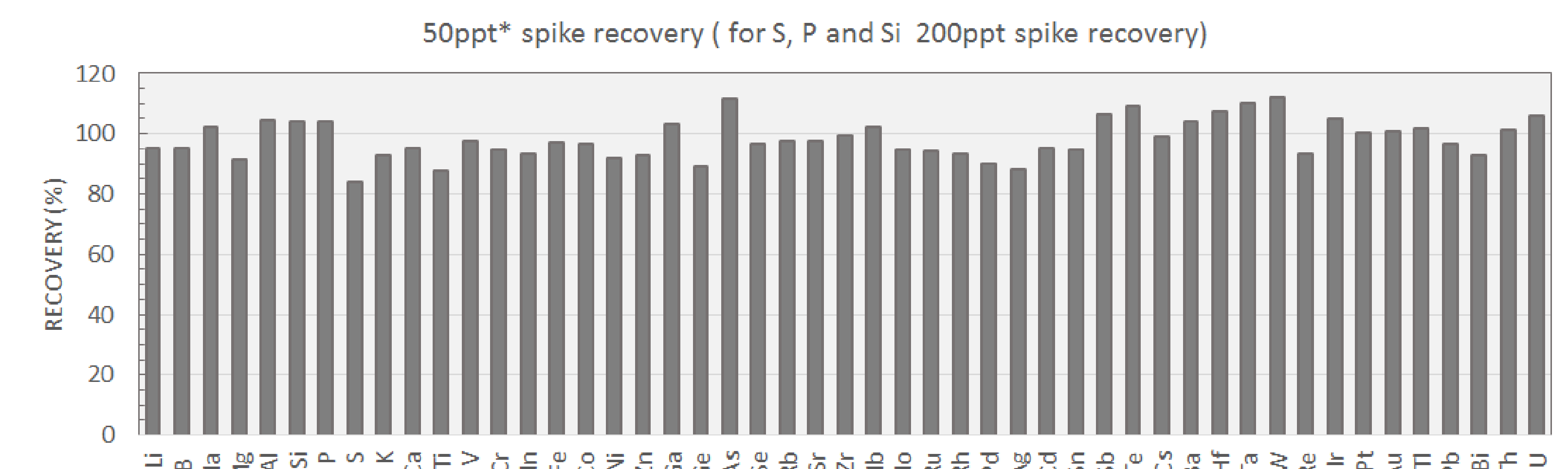

Figure 4 50ppt* spike recovery test (200ppt spike for S, P and Si): Most of elements gave 90-110% recovery and all elements fell within 85-115% recovery.

Conclusions

o Achieved ppt level BEC for alkali metal elements under hot plasma conditions.
o Achieved 100s ppt level BEC for the most challenging elements; Sulfur and Silicon.
o Simple single mode measured all 49 elements in 0.1% high purity Cu sample at ultra low level.