

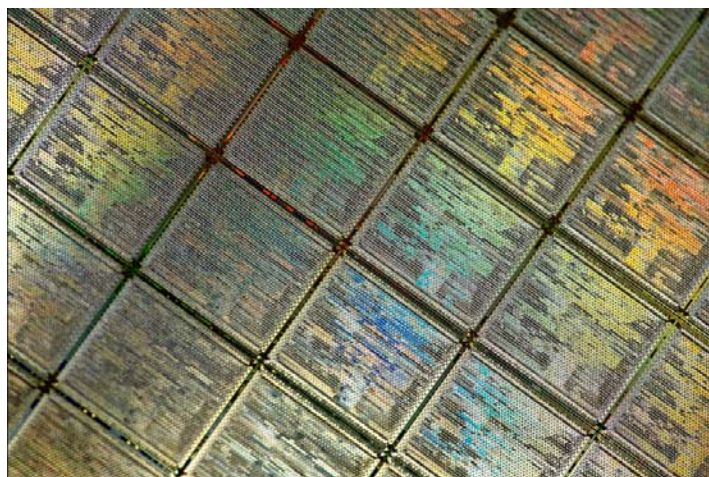
# Direct measurement of metallic impurities in 20% ammonium hydroxide by Agilent 7700s ICP-MS

## Application Note

Semiconductor

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### Abstract

Ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) is a chemical used in the manufacture of semiconductor devices, and must therefore be analyzed for trace metal impurities. The direct analysis of undiluted (20%)  $\text{NH}_4\text{OH}$  using ICP-MS is challenging, because its high vapor pressure causes plasma instability. However, dilution of the samples would degrade detection limits, so the ability to directly analyze 20%  $\text{NH}_4\text{OH}$  is important. The Agilent 7700s ICP-MS employs a unique, high-speed frequency-matching ICP RF generator that can maintain a stable plasma even when 20%  $\text{NH}_4\text{OH}$  is aspirated. The 7700s also features the most effective technologies for removing spectral interferences in high-purity chemicals, making it ideally suited to semiconductor chemical analysis. An Agilent 7700s, using an inert sample introduction system, was used to measure trace elements in high purity 20%  $\text{NH}_4\text{OH}$ . Detection limits in the single digit ppt or sub-ppt range were obtained for 48 elements, and long term (~7 hours) stability of approximately 5% RSD was achieved for a spike level of 100 ppt in 20%  $\text{NH}_4\text{OH}$ , demonstrating the ability of the 7700s to routinely measure trace contaminants in high purity 20%  $\text{NH}_4\text{OH}$ .



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## Introduction

Many chemicals are used throughout the manufacturing process of semiconductor devices. Metallic impurities present in the chemicals and chemical mixes used can cause contamination and give rise to defects in the final product, so their levels must be strictly controlled. ICP-MS is the standard technique used for the measurement of metallic impurities in semiconductor chemicals. Among all the process chemicals, those that are used as part of the silicon wafer cleaning process are particularly important, as they are in direct contact with the wafer and can therefore impart impurities to the wafer surface. There are over 100 cleaning steps throughout the manufacture of a typical semiconductor device, and one of the typical solutions used for wafer cleaning is a chemical mix developed by RCA, commonly referred to as Standard Clean 1 (SC-1). SC-1 is a mixture of  $\text{NH}_4\text{OH}$ , hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ultra-pure water (UPW) in the ratio 1:1:5, and is used to remove surface particles by lightly etching the wafer. There is a clear requirement for a highly sensitive and reliable analytical methodology to measure metallic impurities in the high purity chemicals from which SC-1 is produced.

While UPW and  $\text{H}_2\text{O}_2$  are easy matrices to analyze, the analysis of high purity  $\text{NH}_4\text{OH}$  by ICP-MS is very difficult for two reasons. Firstly,  $\text{NH}_4\text{OH}$  is a strong alkali, which causes some metals to readily precipitate as insoluble hydroxides. This presents difficulties for determination using the method of standard additions (MSA), because MSA is performed by sequentially spiking an acid-based multi-element standard into the sample. At higher concentrations, some metals will precipitate when spiked into the undiluted  $\text{NH}_4\text{OH}$ , making accurate determination by MSA impossible. However, the  $\text{NH}_4\text{OH}$  used in SC-1 is high purity grade with a maximum metallic impurity level of 100 ppt, so higher level spikes can be avoided if the ICP-MS detection limits are sufficiently low. If MSA spikes are at the low ppt level (<100 ppt), minimal precipitation should occur, and MSA can in fact be used to analyze undiluted  $\text{NH}_4\text{OH}$ . To be able to produce good MSA

calibrations below 100 ppt of course requires the interference removal technology employed in the ICP-MS to be extremely effective for all interferences.

The Agilent 7700s ICP-MS, with the third generation Octopole Reaction System (ORS<sup>3</sup>), has the widest range of interference removal technologies of any ICP-MS instrument. In addition to conventional no gas mode, the ORS<sup>3</sup> operates in both collision (He) mode and reaction (e.g.  $\text{H}_2$ ) mode, and cool plasma mode is also available. The interference removal approach selected depends on the analytical requirement: for this application, calibration down to the 10 ppt level is required for all analytes and therefore the most efficient interference removal mode is required for every analyte. Switching between modes is fully automated and all analytes are measured with a single visit to the sample vial. The small size of the ORS cell allows very fast switching between cell gas modes so the additional time required for multi-mode operation is minimized.

The second challenge when analyzing undiluted  $\text{NH}_4\text{OH}$  is that the plasma becomes unstable due to the high vapor pressure of undiluted  $\text{NH}_4\text{OH}$ , so routine, direct analysis of undiluted  $\text{NH}_4\text{OH}$  has not previously been possible. The accepted method of analyzing  $\text{NH}_4\text{OH}$  is to remove the matrix by heating to near dryness and then re-dissolving the residue in 1%  $\text{HNO}_3$  prior to measurement by ICP-MS [1]. Although this method is widely used, laboratories favor elimination of the sample preparation step, to shorten analysis time and reduce the risk of sample contamination and loss of volatile analytes. The Agilent 7700 Series features a unique RF plasma generator design with high-speed frequency-matching that can instantaneously adjust to changes in plasma load – for example when switching from aqueous to a high vapor pressure solvent. This produces a very stable plasma capable of tolerating the direct aspiration of undiluted  $\text{NH}_4\text{OH}$ .

The combination of high sensitivity, effective removal of interferences, and high-speed frequency-matching ICP RF generator enables the Agilent 7700s to measure low ppt level metallic impurities directly in undiluted high purity  $\text{NH}_4\text{OH}$ .

## Experimental

An Agilent 7700s was fitted with an inert sample introduction system (Agilent part # G4912-68002) comprising a PFA double pass spray chamber and demountable torch fitted with a 1.5 mm ID sapphire injector. Standard Pt interface cones and PFA concentric nebulizer were used. A solution of Li, Zn, Sn and Pb prepared in 2% NH<sub>4</sub>OH was used to tune the instrument. These elements were chosen since they form amphoteric oxides or hydroxides (which can display both acidic and basic properties), and are therefore stable in NH<sub>4</sub>OH. The normal tuning solution containing Li, Y, Ce and Tl in 2% nitric acid may also be used, but a thorough rinsing with UPW prior to analysis is necessary to prevent residual acid mixing with the NH<sub>4</sub>OH standard and samples. Once the tuning conditions have been established, the system should be rinsed with UPW and then 20% NH<sub>4</sub>OH for an hour to ensure that the sample introduction system is free from acid. Operating parameters are shown in Table 1. The acquisition used a multi tune mode method, performed with a single visit to the sample vial, and data for each of the modes (cool plasma, no gas, He mode and H<sub>2</sub> mode) was combined automatically into a single report for each sample. Total run time per sample, including uptake and rinse, was 8m 20s.

High purity grade NH<sub>4</sub>OH (20% as NH<sub>3</sub>) was used (TAMAPURE-AA100, TAMA Chemicals, Kawasaki, Japan), and the MSA calibration standard solutions were prepared by spiking a mixed multi-element standard (SPEX CertiPrep, Metuchen, NJ, USA). Calibration levels, added sequentially into a blank of undiluted NH<sub>4</sub>OH, were at 10, 20, 50 and 100 ppt.

## Results

### DLs and BECs

3  $\sigma$  detection limits (DLs) and background equivalent concentrations (BECs) obtained for 48 elements in high purity NH<sub>4</sub>OH are shown in Table 2. For Se and Te, the lowest detection limits were obtained using H<sub>2</sub> mode, while for Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni and Cu, cool plasma mode was used. For the remainder, He mode was used except for Be and B which were run using no gas mode. The DLs were calculated from 10 measurements of the blank. All DLs were single figure ppt or lower, as were the BECs, aside from Ca at 11 ppt. This demonstrates the ability of the 7700s to remove spectral interferences, and also the high quality of this NH<sub>4</sub>OH product. Since no individual analysis mode gives the ultimate DLs for every element, the 7700s offers the ultimate performance for semiconductor chemical analysis by allowing the user to automate analysis methods with no gas, He and H<sub>2</sub> modes, plus cool plasma. This flexibility, coupled with pre-defined methods and simple, automated optimization routines makes the 7700s the most powerful ICP-MS for semiconductor analysis.

**Table 1:** 7700s Operating Parameters

	Normal Plasma	Cool Plasma
Forward power (W)	1600	600
Carrier gas (L/min)		0.8
Make up gas (L/min)	0.1	0.5
Sampling depth (mm)	7	18
Cell gas flow (mL/min)		
He mode	5	-
H <sub>2</sub> mode	6	-
Cell KED (V)	3	-
Uptake time (s)		60
Acquisition time (s)		350
Rinse time (s)		90

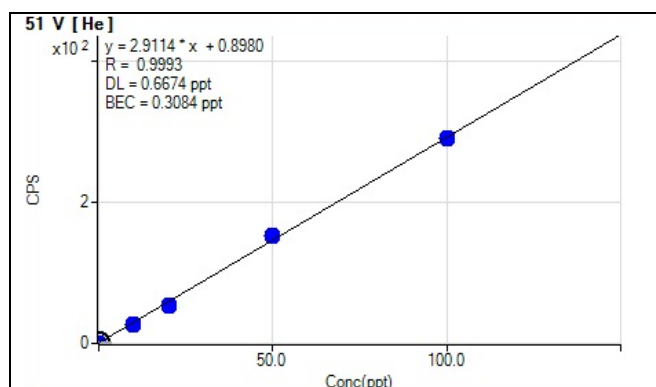
**Table 2:** 7700s ICP-MS DLs and BECs in 20% NH<sub>4</sub>OH

Element	m/z	Mode	DL/ppt	BEC/ppt
Li	7	cool	0.014	0.003
Be	9	no gas	0.33	0.1
B	11	no gas	2.6	16
Na	23	cool	0.43	0.38
Mg	24	cool	0.17	0.32
Al	27	cool	0.26	0.67
K	39	cool	0.25	0.38
Ca	40	cool	1.9	11
Ti	48	He	2.4	1.4
V	51	He	0.67	0.31
Cr	52	cool	0.3	0.4
Mn	55	cool	0.078	0.026
Fe	56	cool	1.5	2.1
Co	59	cool	0.23	0.052
Ni	60	cool	0.88	0.42
Cu	63	cool	3	1.8
Zn	66	He	1.7	0.8
Ga	71	He	1.7	0.68
Ge	72	He	4.3	1.6
As	75	He	6.5	3.8
Se	78	H <sub>2</sub>	8.4	4.6
Rb	85	He	0.022	0.028
Sr	88	He	0.86	0.29
Zr	90	He	0.35	0.2
Nb	93	He	0.057	0.076
Mo	98	He	0.24	0.16
Ru	101	He	0.26	0.1
Rh	103	He	0.41	1.4
Pd	105	He	0.18	0.092
Ag	107	He	0.11	0.12
Cd	111	He	0.66	0.35
Sn	118	He	2.3	1.5
Sb	121	He	2.3	0.92
Te	125	H <sub>2</sub>	1.3	1.3
Cs	133	He	0.41	0.21
Ba	138	He	0.27	0.13
Hf	178	He	0.24	0.086
Ta	181	He	0.047	0.036
W	182	He	0.16	0.071
Re	185	He	0.14	0.061

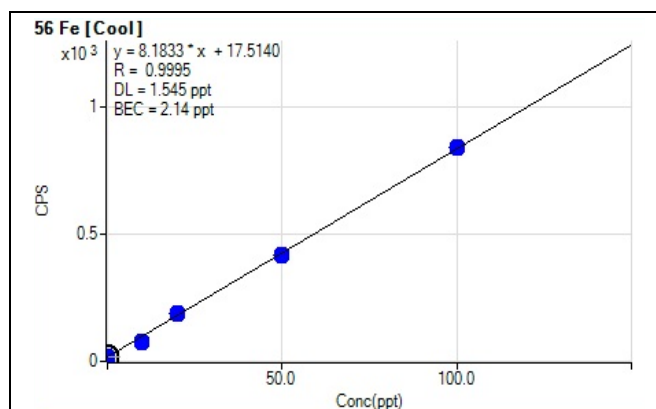
Element	m/z	Mode	DL/ppt	BEC/ppt
Ir	193	He	0.15	0.16
Pt	195	He	0.39	0.48
Au	197	He	0.4	0.17
Tl	203	He	0.21	0.27
Pb	208	He	0.75	1.1
Bi	209	He	0.16	0.15
Th	232	He	0.085	0.025
U	238	He	0.064	0.013

## Calibration linearity

Figures 1a and 1b show examples of the calibration plots achieved for elements in two different modes: V (He mode) and Fe (cool plasma mode). Excellent linearity at the ppt level was achieved in each case, demonstrating the interference removal power of the 7700s in both modes.



**Figure 1a:** Calibration plot showing spikes at 0, 10, 20, 50 and 100 ppt for V in 20% NH<sub>4</sub>OH



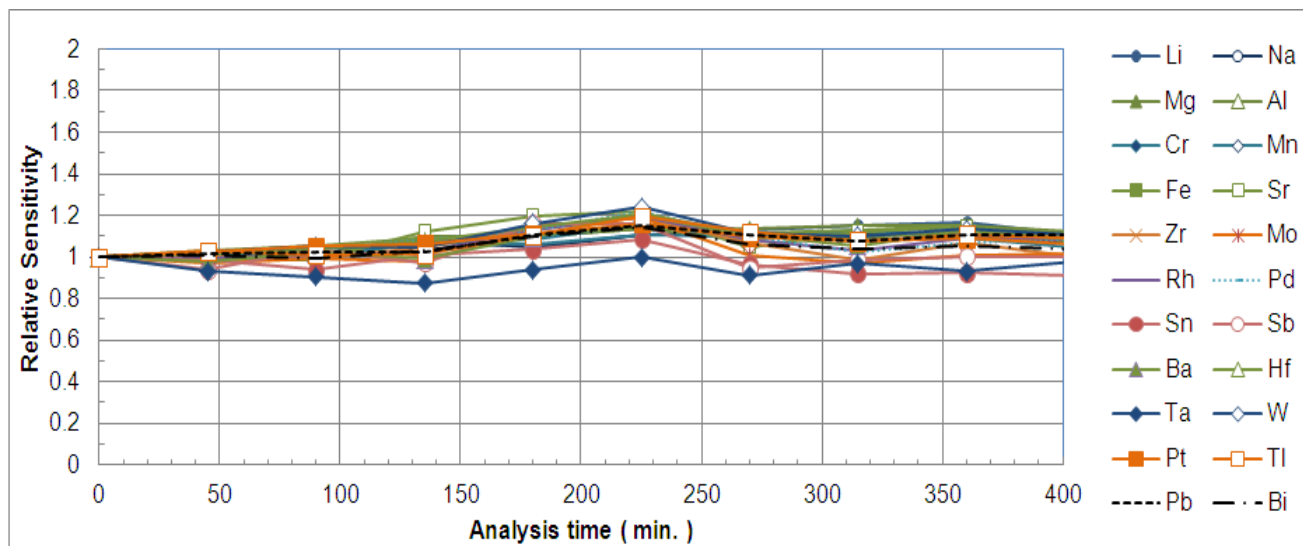
**Figure 1b:** Calibration plot showing spikes at 0, 10, 20, 50 and 100 ppt for Fe in 20% NH<sub>4</sub>OH

## Long term stability

If present at a high enough concentration in an alkaline solution, many metals form insoluble hydroxides which easily form precipitates or can be adsorbed on to the surface of the vessel wall, and the likelihood of precipitation or adsorption increases with time. Keeping metal concentrations low (at a maximum of 100 ppt) reduces the risk of precipitation, and monitoring signal stability over an extended period is an effective way to confirm the chemical stability of the analytes. A long term (just under 7 hours) stability test was performed for 22 elements spiked at 100 ppt in 20%  $\text{NH}_4\text{OH}$ . Signal intensity was measured every 45 min while blank samples of 20%  $\text{NH}_4\text{OH}$  were introduced between each spike measurement. Figure 2 shows the excellent stability (approx. 5% RSD) of the spikes over the test period, confirming the applicability of direct analysis using MSA at spike concentrations up to the 100 ppt level in 20%  $\text{NH}_4\text{OH}$ .

## Conclusions

The direct analysis of 20%  $\text{NH}_4\text{OH}$  was performed successfully using an Agilent 7700s ICP-MS. The high speed frequency-matching RF generator of the 7700 produces a stable plasma when 20%  $\text{NH}_4\text{OH}$  is aspirated, while the availability of multiple interference removal technologies assures low DLs and BECs for all 48 elements measured. The routine applicability of direct measurement using MSA has been demonstrated by limiting spike concentrations to 100 ppt, which avoids precipitation in the alkaline matrix. As a result, labs are no longer forced to carry out matrix removal in order to analyze high purity 20%  $\text{NH}_4\text{OH}$  by ICP-MS, and direct analysis is routinely possible.



**Figure 2:** Signal stability of a representative selection of 22 elements spiked at 100 ppt in 20%  $\text{NH}_4\text{OH}$

## References

1. Takeda K., Ikushima S., Okuzaki J., Watanabe S., Fujimoto T., Nakahara T., *Anal. Chim. Acta* 426, 1, 105, 200

[www.agilent.com/chem](http://www.agilent.com/chem)

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