



Analytical note

## Accurate determination of non-metallic impurities in high purity tetramethylammonium hydroxide using inductively coupled plasma tandem mass spectrometry

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## ABSTRACT

The content of non-metallic impurities in high-purity tetramethylammonium hydroxide (HPTMAH) aqueous solution has an important influence on the yield, electrical properties and reliability of the integrated circuit during the process of chip etching and cleaning. Therefore, an efficient analytical method to directly quantify the content of non-metallic impurities in HPTMAH aqueous solutions is necessary. The present study was aimed to develop a novel method that can accurately determine seven non-metallic impurities (B, Si, P, S, Cl, As, and Se) in an aqueous solution of HPTMAH by inductively coupled plasma tandem mass spectrometry (ICP-MS/MS). The samples were measured using a direct injection method. In the MS/MS mode, oxygen and hydrogen were used as reaction gases in the octopole reaction system (ORS) to eliminate mass spectral interferences during the analytical process. The detection limits of B, Si, P, S, Cl, As, and Se were 0.31, 0.48, 0.051, 0.27, 3.10, 0.008, and 0.005  $\mu\text{g L}^{-1}$ , respectively. The samples were analyzed by the developed method and the sector field inductively coupled plasma mass spectrometry (SF-ICP-MS) was used for contrastive analysis. The values of these seven elements measured using ICP-MS/MS were consistent with those measured by SF-ICP-MS. The proposed method can be utilized to analyze non-metallic impurities in HPTMAH aqueous solution.

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## 1. Introduction

High-purity-tetramethylammonium hydroxide (HPTMAH), a highly water-soluble and alkaline organic solvent, is one of the most important basic chemicals used in the production of integrated circuits (IC), very large scale integrated circuits (VLSI) and discrete devices [1]. It is usually prepared as a 25% aqueous solution, and mainly used as a cleaning agent for integrated circuit and an etching agent in semiconductor micro-processing technology [2–4]. With continuous scale expansion and decrease in the line-width of integrated circuits, the stringency of the quality requirements for HPTMAH aqueous solution have increased. Relevant standards for HPTMAH aqueous solution have been formulated by Semiconductor Equipment and Materials International (SEMI) on the basis of the line-width range of integrated circuit, which suggests that the metallic and non-metallic impurity content of HPTMAH aqueous solution should be minimal [5]. Therefore, accurate determination of the impurities in HPTMAH aqueous solution is critical.

Inductively coupled plasma mass spectrometry (ICP-MS) is the favorite method of estimating impurities in HPTMAH aqueous solutions because of the capability of ICP-MS to perform rapid multi-elemental

analysis of trace and ultra-trace elements in complex samples [6–8]. However, determination of non-metallic impurities in HPTMAH aqueous solution by ICP-MS still faces many challenges. Non-metallic impurities have high first ionization potential (IP), low ionization efficiency in inductively coupled plasma (ICP), and low content in the sample, which significantly reduce the analytical signals. The sensitivities of these elements are relatively lower than those of other general elements (elements with IP of ~6–8 eV). Conventional ICP-MS (ICP-QMS) cannot eliminate the matrix element-generated polyatomic ion interferences generated completely. The matrix suppression of high carbon containing organic matters affects the accuracy of the analytical results, especially the direct analysis of organic samples.

The octopole reaction system (ORS) technique can effectively eliminate mass spectral interferences [9]. In collision mode, the elimination of interfering ions are based on kinetic energy discrimination (KED), which would reduce analyte sensitivity, and thus, the process is not suitable for the determination of hard-to-ionize non-metallic elements [10]. In reaction mode, ICP-MS has higher ability to remove interference than collision mode for trace elements; however, the byproduct ions formed due to unpredictable reaction processes may affect the accuracy of the analysis [11]. Therefore, precise control over reaction processes and reaction products are important for operation of this reaction mode. Inductively coupled plasma tandem mass spectrometry (ICP-

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MS/MS) was equipped with a new quadrupole mass analyzer ( $Q_1$ ) in front of ORS, which can filter the fragment ions entering the ORS by setting the specified mass-to-charge ratio ( $m/z$ ) to control the chemical reactions of ions/molecules in the ORS. A second quadrupole mass analyzer ( $Q_2$ ) was placed behind the ORS to eliminate the interfering ions from  $Q_1$  [12–15]. Addition of  $Q_1$  significantly improved the sensitivity compared to the traditional ICP-MS [16]. In the MS/MS mode (simultaneous running  $Q_1$  and  $Q_2$ ) of ICP-MS/MS, oxygen (one of the most commonly used reaction gases) has been successfully used to eliminate various complex mass disturbances by mass-shift or charge transfer [12,15,17–19]. Hydrogen is not a highly reactive gas, has affinity for highly electronegative atoms, can capture the latter from metastable molecular ions, thus eliminating the interference [20,21]. In addition, the use of  $NH_3$  and  $CH_3F$  as reaction gases for eliminating interference has also been reported [13,22–24]; however,  $NH_3$  is not suitable as a reaction gas for the analysis of non-metallic elements.

In this study, the content of seven non-metallic elements (B, Si, P, S, Cl, As, and Se) were estimated in HPTMAH aqueous solution by ICP-MS/MS using the direct injection method. In the MS/MS mode,  $O_2$  and  $H_2$  were used as reaction gases to eliminate the interference. This method provides an accurate analysis for the quality control of HPTMAH aqueous solutions.

## 2. Experimental

### 2.1. Instrumentation

All the measurements were performed using an Agilent 8800 ICP-MS/MS (Agilent, USA), equipped with a narrow injector (id = 1.5 mm) torch typically used for the analysis of organic solvents. The injection system consisted of inert components, including a C-flow 200 PFA concentric nebulizer with a double-pass PFA spray chamber cooled to 0 °C, and an online internal standard (ISTD) mixing kit.

Direct injection of organic samples into ICP would increase the load and affect the stability of the ICP [25]. The ionization of non-metallic elements (B, Si, P, S, Cl, As, and Se) in the ICP requires higher plasma temperature than the general analytical conditions. Therefore, the plasma conditions have to be optimized manually to achieve the maximum ionization efficiency while the ICP is maintained under stable conditions. The ICP temperature can be increased by increasing the RF power of the instrument to 1550 W and reducing the makeup gas flow rate to 0.1 L min<sup>-1</sup>. The high background signals formed by high RF power can be eliminated by selecting the dual mass-to-charge ratio ( $m/z$ ) function in the MS/MS mode. The operating conditions of ICP-MS/MS are shown in Table 1. During this method, the reaction gases ( $O_2$  or  $H_2$ ) were passed through the ORS for preconditioning (for 30 s) to ensure a smooth replacement of the gas during the conversion of the different cell gas modes. To prevent the formation of carbon deposit, 20% (v/v)  $O_2$  was added to the carrier gas via an option gas flow line to prevent carbon build up.

**Table 1**  
Operating conditions of Agilent 8800 ICP-MS/MS.

Parameters	Setting
Scan type	MS/MS
RF power	1550 W
Plasma gas flow rate	18 L min <sup>-1</sup>
Carrier gas flow rate	1.05 L min <sup>-1</sup>
Make up gas flow	0.10 L min <sup>-1</sup>
Cell gas	$O_2$ , $H_2$
$O_2$ flow rate	0.40 mL min <sup>-1</sup>
$H_2$ flow rate	4.5 mL min <sup>-1</sup>
Selected mass at $Q_1$	11, 28, 31, 32, 35, 75, 78
Selected mass at $Q_2$	11, 28, 47, 48, 37, 91, 94
Octopole bias voltage	−18 V ( $O_2$ mass shift), −10 V ( $H_2$ mass shift and $H_2$ on mass)
KED bias voltage	−7 V ( $O_2$ mass shift), 0 V ( $H_2$ mass shift and $H_2$ on mass)

To evaluate the accuracy of this method, all the samples were also analyzed using Element XR sector field (SF) ICP-MS (Thermo Scientific, USA) as a control. The operational conditions of SF-ICP-MS are listed in Table S1 (Appendix A). Ultrapure water (resistivity higher than 18.2 MΩ cm) prepared using a Milli-Q-ultrapure system (Millipore, USA) was utilized throughout the experiment.

### 2.2. Reagents and standards

Working standard solutions were prepared by adequate dilution of 10 mg L<sup>-1</sup> B, Si, P, S, Cl, As, and Se stock solutions (Merck, Germany). The ISTD mixed solution of 1 mg L<sup>-1</sup> was prepared by adequate dilution of 10 mg L<sup>-1</sup> Be, Sc, and Ge stock solutions (Merck, Germany).

### 2.3. Samples and sample analysis

Electronic grade HPTMAH aqueous solutions (25%) were purchased from different sources in China (Shanghai, Shenzhen, Nantong, and Suzhou). The sample has not undergone any treatment before the injection. The ISTD solution was on-line mixed with the sample solutions using a T- junction and analyzed under optimized experimental conditions.

A series of mixed standard solutions containing B, Si, P, S, Cl, As, and Se were prepared using ultrapure water. The solutions were measured under the optimized experimental conditions. The calibration curve, automatically created by the instrument, was used to calculate the concentration of B, Si, P, S, Cl, As, and Se in the sample solutions.

## 3. Results and discussion

### 3.1. Selection of analysis mode

The content of non-metallic impurities in highly pure organic matter is low, while interferences from C, O, N, and H of the organic matrix render analysis of these elements challenging. All the analytically useful isotopes were affected by multiple spectral interferences [26] as summarized in Table S2 (Appendix A). The effects of B, Si, P, S, Cl, As, and Se in the single quadrupole (SQ,  $Q_1$  only as ion channel, similar to the commonly used ICP-QMS equipped with ORS) mode were investigated using He as the collision gas, and  $H_2$  and  $O_2$  as the reaction gas in the MS/MS mode, and the sensitivity, background equivalent concentration (BEC), and detection limit (DL) of preferable isotopes of B, Si, P, S, Cl, As, and Se were studied. As can be seen from Table 2, Si and S could not be measured at the spiked concentrations using helium as the collision gas with SQ mode, and the sensitivity of detecting B was lower than that obtained when  $H_2$  is used as the reaction gas in the MS/MS mode. The sensitivity of P detection was lower than that obtained when  $O_2$  is used as the reaction gas in the MS/MS mode, and the sensitivity of Cl, As, and Se were lower than those observed in the MS/MS mode, while the BEC and DL of all elements were higher than those obtained in the MS/MS mode. This was due to the low ionization efficiency of these nonmetallic elements. The energies of these elements were lost significantly due to the collision dissociation or KED during the helium collision process, leading to low sensitivity and inaccurate analysis. The spiked concentrations of P and S cannot be determined using hydrogen as the reaction gas in the SQ mode. Reports show that since the usage of Xe as a reaction gas can effectively reduce the interference in the determination of S without significantly reducing the background, the process cannot be utilized to effectively determine S [27]. Although the use of ICP-QMS equipped with ORS could eliminate or alleviate certain spectral interferences, some tricky interferences that are difficult to remove persist.

In the MS/MS mode, the reactions of  $^{11}B^+$  with both  $H_2$  and  $O_2$  were endothermic ( $\Delta H_r^\circ > 0$ ), and hence very few product ions were formed. In this study, the on-mass method was used by setting  $Q_1 = Q_2 = 11$ . The double mass selection was adopted to eliminate the overlapped

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