RESEARCH ARTICLE

Direct Determination of Gold in Rock Samples Using Collision Cell Quadrupole ICP-MS

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Abstract

This study investigated the determination of Au in rock samples using collision cell quadrupole inductively coupled plasma mass spectrometry (ICP-MS). It is essential to remove various interferences using a collision cell because polyatomic ions such as $^{181}\text{Ta}^{16}\text{O}^+$ and $^{180}\text{Hf}^{16}\text{O}^{16}\text{H}^+$ can interfere with the direct determination of monoisotopic ^{197}Au when using ICP-MS. The addition of oxygen as a reaction gas removed isobaric interferences by transforming TaO^+ and HfOH^+ to TaO_2^+ , TaO_3^+ , and HfO_2H^+ , HfO_3H^+ , respectively, in the cell without significant Au^+ loss. The ion kinetic energy effect (IKEE) due to the potential difference between the plasma and the hexapole affected the reactions in the cell. Au and interfering ions were very sensitive to cell bias voltage (V_c) at constant plasma potential (V_p) and quadrupole bias voltage (V_q). Under the condition of hot plasma, the transmission of ions was promoted, and the maximum Au signal intensity was 50% greater than under normal conditions. At $V_c > 7$ V, TaO^+ ions were removed to background level. Optimized conditions for real sample analysis were obtained by introducing He as an additional collision gas in hot plasma. TaO^+ ions were removed to background level at He flow rates above 0.6 mL min^{-1} , and the Au signal remained high. The detection limit (three times the standard deviation of the blank) of this method was 3.06 pg g^{-1} . The results for reference materials (STM-1 and DGPM-1) and spiked samples showed good agreement between specified and measured concentrations.

Key words: Collision cell, Ion kinetic energy effect, Cell bias voltage, Quadrupole bias voltage

Introduction

To explore geochemistry and to conduct increasingly sophisticated Au deposit assessment procedures, high-quality analytical data are necessary, especially for Au concentrations near or below the cut-off grade. Estimates of crustal abundance are on the order of 0.003–0.004 parts per million [1], and it is very difficult to quantify Au accurately at such low levels. Analytical methods for Au detection include a fire assay [2–5] with instrumental neutron activation (INAA) [2–6], aqua regia dissolution [2, 5, 6] with atomic absorption (AA) such as graphite furnace atomic absorption (GFAA), aqua regia dissolution with inductively

coupled plasma mass spectrometry (ICP-MS), and a combination of cyanidation [2] and AA, GFAA, or ICP-MS. Additional methods include ion exchange [7, 8], pre-concentration, and vapor generation with inductively coupled plasma atomic emission spectrometry (ICP-AES) [9].

Aqua regia dissolution/ICP-MS is very simple and cost effective. Furthermore, it can quantitatively recover gold in rock samples [6] due to the excellent detection ability of ICP/MS. However, aqua regia dissolution without a separation procedure suffers from several polyatomic interferences during ICP-MS analysis. Oxides and hydroxides of matrix metals such as $^{181}\text{Ta}^{16}\text{O}^+$ and $^{180}\text{Hf}^{16}\text{O}^{16}\text{H}^+$ interfere with the monoisotope ^{197}Au [6, 10–12]. Although this can be corrected using mathematical equations that include $^{181}\text{Ta}^{16}\text{O}^+ / ^{181}\text{Ta}^+$ and $^{180}\text{Hf}^{16}\text{O}^{16}\text{H}^+ / ^{180}\text{Hf}^+$ ratios, the results for ^{197}Au analysis have large errors because both Ta and Hf concentrations are thousands of times higher than Au in rock

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samples. Therefore, for the direct determination of ^{197}Au using ICP-MS, it is essential to remove interferents using a technique such as a collision cell procedure.

Collision cell technology uses collision/reaction gases such as H_2 , He , O_2 , NH_3 , or CH_4 to remove polyatomic interferents in ICP-MS through collisional removal or transformation to other interfering ions. For Au analysis, several studies have suggested the use of O_2 as a reaction gas for the transformation of TaO^+ and HfOH^+ to heavier compounds such as TaO_2^+ and HfO_2H^+ [11, 13–16], respectively. However, optimization of Au analysis by removing interfering ions using collision cell technology for rock samples with very low Au concentrations and high Ta and Hf concentrations has not yet been reported.

This study investigated the effects of collision/reaction gases and instrumental parameters controlling ion energy in hexapole collision cell ICP-MS and determined Au concentrations directly in rock samples containing high Ta and Hf concentrations without pre-concentration procedures.

Experimental

Background on Collision Cell Technology

Ions produced in the plasma enter the interface, where they are extracted under vacuum into a collision cell that is positioned before the analyzer quadrupole. Collision/reaction gases such as H_2 , He , O_2 , NH_3 , or CH_4 are then bled into the cell, which consists of a multipole (a quadrupole, hexapole, or octapole), usually operated in radio frequency (rf)-only mode. The rf-only field does not separate the masses like a traditional quadrupole but instead focuses the ions, which then collide and react with molecules of the collision/reaction gas. By a number of different ion–molecule collision and reaction mechanisms, polyatomic interferents such as argides (e.g., Ar_2^+ , ArCl^+ , ArN^+ , ArH^+ , ArC^+) and oxides (e.g., CaO^+ , ZnO^+ , CeO^+ , ZrO^+ , TaO^+) derived from the plasma gas, matrix components, or an acid used to dilute a solution are converted to harmless, non-interfering species, or the target ions are converted to other ions. The target ions, free from the interference, then emerge from the collision cell and enter the quadrupole analyzer for normal mass separation [11, 14].

Kinetic energy discrimination (KED) is the key to distinguishing the collision product ions from target ions. This is achieved by setting the collision cell bias slightly less positive than the quadrupole bias. This means that the collision product ions, having the same energy as the cell bias, are discriminated against and rejected, while the analyte ions, having a higher energy than the cell bias, are transmitted [13, 17–23]. Because polyatomic ions collide with collision gas more frequently than with analyte ions, most of the analytes maintain a higher energy than the collision product ions.

Early work by Tuner et al. using He gas alone in a collision cell resulted in the successful attenuation of the argide ions Ar_2^+ , ArCl^+ , ArO^+ , and Ar^+ , enabling the quantification of Se, As, Fe, and Ca [24]. Feldmann et al.

reduced $^{40}\text{Ar}^{40}\text{Ar}^+$ ions, allowing the detection of ^{80}Se at sub-part per billion levels [26].

Du and Houk also described the attenuation of metal oxides (ZrO^+ , CeO^+ , LaO^+ , SmO^+ , HoO^+ , YbO^+ , and WO^+) by dissociation using H_2 gas [19]. While most polyatomic ions are weakly bound, TaO^+ (dissociation energy = $\sim 750 \text{ kJ mol}^{-1}$) and HfOH^+ are strongly bound and do not easily dissociate into single ions, although sufficient collision gas can be supplied [14]. Furthermore, Ta and Hf exist in much higher concentrations than Au in rock, and collision is not able to break polyatomic ions that interfere with Au^+ ; excess collision gas removes Au^+ .

Fortunately, TaO^+ and HfOH^+ with higher internal energies than Au^+ can react with O_2 gas and are easily transformed into TaO_2^+ , TaO_3^+ and HfO_2H^+ , HfO_3H^+ , respectively, but Au^+ does not react with O_2 gas and is not transformed [11, 13–16]. As a result, O_2 reaction gas in a collision cell makes it possible to distinguish polyatomic interferents such as TaO^+ and HfOH^+ from an analyte, in this case Au^+ .

Instrumentation

In this study, a quadrupole-based ICP-MS instrument (Thermo Elemental, X7, Manchester, UK) with a hexapole collision cell operated in Korea Basic Science Institute was used (Scheme 1). The collision cell was positioned between the extraction lens and ion lens, followed by the quadrupole. The ions formed in the argon plasma at atmospheric pressure were accelerated by applying a negative potential (-497 V) to the extraction lens and were transported through the hexapole mass analyzer. O_2 was introduced into the collision cell as a reaction gas and He was used as a collision gas. These gases were controlled by mass flow controllers using the software for X-7. Two types of plasma modes were used to make two kinds of plasma potentials: one is a standard mode which is made using normal plasma conditions, and the other is a hot plasma mode which use metal screen between quartz torch and load coil to reduce the plasma potential and to make a narrow ion energy distribution [25]. The Meinhard concentric nebulizer and a quartz spray chamber cooled to 3°C using a Peltier cooling system were used for sample introduction. To reduce the high memory effect of Au, 10% hydrochloric acid was used as a cleaning solution [26]. Details of the instrumental components, typical operating conditions, and data acquisition parameters are given in Table 1.

Reagents and Materials

ICP-MS standard solutions were prepared by serial dilutions of $1000 \mu\text{g mL}^{-1}$ stock standard solution (99.999%; Anapure Ltd. Daejeon, Korea). High-purity deionized water (resistivity higher than $18 \text{ M}\Omega \text{ cm}^{-1}$) was obtained from a Milli-Q Plus water purifier (Millipore, Bedford, MA, USA). High-purity acids for sample pretreatment were purchased from Dongwoo Pure Chemicals (electronic grade; Iksan,

Scheme 1. Schematic diagram of hexapole collision cell QICP-MS

Korea), and HNO_3 was purified using the Teflon two-bottle method for sub-boiling distillation in the laboratory. Reference materials STM-1 and DGPM-1 were purchased from the U.S. Geological Survey (Denver, CO, USA). STM-1 is the standard reference material of nepheline syenite containing $28 \pm 2 \mu\text{g g}^{-1}$ Hf and $18.6 \pm 1.2 \mu\text{g g}^{-1}$ Ta, and DGPM-1 is a disseminated gold ore reference material containing $0.730 \pm 0.060 \mu\text{g g}^{-1}$ Au used to establish analytical accuracy for the determination of gold. All bottles used in this study were thoroughly pre-cleaned by soaking in 10% hydrochloric acid for several days. O_2 and He gases were obtained from Daeil Science (99.999%; Daejeon, Korea).

Sample Preparation

Spiked Samples

Different amounts of Au standard solution were spiked in 10 ng g^{-1} Ta and Hf mixed solutions to prepare seven spiked

samples (Au concentration: $\sim 4.7\text{--}756 \mu\text{g g}^{-1}$), which resulted in $\sim 12\text{--}2,000$ Ta/Au and Hf/Au ratios.

Reference Materials

Reference materials were mixed at STM-1:DGPM-1 weight ratios of 1:1, 1:2, 1:3, 1:4, and 1:5. All mixed materials were dried sufficiently in desiccators. Approximately 0.2 g of mixed material was put in a Teflon digestion vessel (60 mL; Savillex Co., MN, USA), and then 4 mL aqua regia, 2 mL Hf, and 1 mL HClO_4 were added. After the mixed materials were decomposed entirely by heating on a hot plate at 150°C overnight, each solution was evaporated. Then 2 mL 4:4:1 HNO_3 :Hf: HClO_4 mixed acid was added and heated at 150°C overnight. After this solution was evaporated, residues were dissolved in 5% HNO_3 and diluted to 200 g using 5% HNO_3 . This solution was filtered and introduced to the ICP-MS.

Results and Discussion

Optimization of Instrumental Conditions

Using a collision cell ICP-MS to analyze Au in rock samples, interferences such as TaO^+ and HfOH^+ induced from the sample matrix were removed by reaction with O_2 and collision with He. Instrumental conditions, including O_2 and He gas flow rates, ion energy effects with respect to plasma potential, collision cell bias, and quadrupole bias, were optimized to obtain the maximum Au signal and minimum interferences.

Effect of O_2 Reaction Gas

Only O_2 gas was introduced into the collision cell for this investigation to determine the effect of O_2 reaction gas using 1 ng g^{-1} Au, 50 ng g^{-1} Ta, and 50 ng g^{-1} Hf solutions (Figures 1 and 2). Before adding O_2 gas, TaO^+ existed at an intensity of about 0.7% of that of Ta^+ . At O_2 flow

Table 1. Optimum operating parameters used for Au measurement using collision cell quadrupole ICP/MS

ICP		
Spray chamber temperature ($^\circ\text{C}$)	3	
Sample uptake rate (mL min^{-1})	0.4	
Forward power (W)	1250	
Reflected power (W)	<2	
Argon flow rate		
Cooling gas (L min^{-1})	13.1	
Auxiliary gas (L min^{-1})	0.66	
Nebulizer gas (L min^{-1})	0.96	
Collision cell		
Oxygen gas (mL min^{-1})	0.4	0.4
Helium gas (mL min^{-1})	—	0.66
Cell bias voltage (V)	9.9	5.5
Ion optics		
Extraction lens voltage (V)	−497	−733
Focus (V)	20.3	15.9
Lens 1 (V)	4.2	−2.3
Lens 2 (V)	−157.5	−57.2
Lens 3 (V)	−174.5	−144.1
Quadrupole bias voltage (V)	1.0	−2.0

Figure 1. Influence of O₂ flow rate on (a) Ta⁺ and Ta oxide species for the introduction of 50 ng g⁻¹ Ta solution and (b) Au⁺ for the introduction of 1 ng g⁻¹ Au solution and the calculated ratio of Au⁺ to TaO⁺ from Au⁺ and TaO⁺ intensities measured by introduction of 1 ng g⁻¹ Au solution and 50 ng g⁻¹ Ta solution, respectively. Cell bias voltage = 9.9 V, quadrupole bias voltage = 1.0 V

rates < 0.05 mL min⁻¹, all Ta oxides increased immediately, and TaO⁺ was the major oxide ion. At increased O₂ flow rates, Ta⁺ ions reacted with O₂ rapidly and transformed into TaO⁺, TaO₂⁺, and TaO₃⁺, but TaO also transformed into TaO₂⁺. Thus, TaO₂⁺ was the major Ta species at O₂ flow rates > 0.1 mL min⁻¹.

Before adding O₂ gas, HfOH⁺ existed at an intensity of about 0.07% that of Hf⁺. The reaction of Hf⁺ ions with O₂ showed a similar trend as those of Ta⁺ and TaO⁺ ions with O₂ (Figure 2) but differed slightly because Hf⁺ and HfOH⁺

reacted with O₂ and presumably residual H₂O or H₂, and then Hf⁺ transformed into HfO₂H⁺ and HfO₃H⁺ via HfOH⁺. HfO₂H⁺ remained as the major Hf-species ion at increased O₂ gas flow rates.

Au⁺ increased rapidly with O₂ flow rates < 0.1 mL min⁻¹ and then decreased gradually with increasing O₂ flow rates. The decrease in the Au⁺ signal was due to collision with O₂ rather than reaction. Excess O₂ also removed many ions by collision. As shown in Figure 3, the reactivity of Ta differed from that of Au with O₂. When the mixed solution

Figure 2. Influence of O₂ flow rate on (a) Hf⁺ and Hf oxide species for the introduction of 50 ng g⁻¹ Hf solution and (b) Au⁺ for the introduction of 1 ng g⁻¹ Au solution and the calculated ratio of Au⁺ to HfOH⁺ from Au⁺ and HfOH⁺ intensities measured by introduction of 1 ng g⁻¹ Au solution and 50 ng g⁻¹ Hf solution, respectively. Cell bias voltage = 9.9 V, quadrupole bias voltage = 1.0 V

Figure 3. Intensity variation in Au^+ and TaO^+ measured by introduction of 1 ng g^{-1} Au solution and 50 ng g^{-1} Ta solution, respectively, as a function of O_2 flow rate. Cell bias voltage = 9.9 V , quadrupole bias voltage = 1.0 V

containing 10 ng g^{-1} Ta and 1 ng g^{-1} Au was introduced, Ta^+ was removed by reaction with O_2 , but Au^+ remained. Due to the sudden decrease in TaO^+ via reaction with O_2 , the intensity of mass number 197 was consistent with 1 ng g^{-1} Au solution at O_2 gas flow rates $> 0.4 \text{ mL min}^{-1}$. Thus, it is suggested that most TaO^+ ions were transformed into other oxides by reaction with O_2 , but Au^+ was affected by collision rather than reaction.

Effect of Relative Ion Energy

The effects of ion energy in a collision cell ICP-MS are key determinants of oxide removal from an analyte. The input ion energy, as determined by the potential difference between the plasma and hexapole, affects the reactions in the collision cell. This is termed the ion kinetic energy effect (IKEE) [13]. If the quadrupole bias voltage (V_q) is more positive than the cell bias voltage (V_c), another ion energy effect, kinetic energy discrimination (KED), which is defined as an exclusion of slow ions formed in a cell, can be applied. In this study, discrimination/rejection of interfering ions (TaO^+ and HfOH^+) with a lower energy than V_q was considered as the removal mechanism of interfering ions in addition to transformation into other oxides (TaO_2^+ , TaO_3^+ , HfO_2H^+ , and HfO_3H^+) by reaction with O_2 . Therefore, ion energy effects depend on the combination of the plasma potential (V_p) and V_c as well as the combination of V_c and V_q . TaO^+ , HfOH^+ , and Au^+ signals showed unique trends with respect to each factor. To identify the influence of each factor on ion energy effects, Au^+/TaO^+ and $\text{Au}^+/\text{HfOH}^+$ ratios and the Au^+ signal were varied by changing each factor under constant operating conditions.

Specifically, a hot plasma with a shield torch at normal rf power was applied to change the plasma offset potential (V_p), which can be used to evaluate the influences of IKEE on TaO^+ and HfOH^+ removal and the Au signal.

Cell Bias Voltage

Figure 4 shows the measured Au^+/TaO^+ ratio and Au^+ signal as a function of V_c . Because V_p and V_q were constant, the variation in V_c indicates the changes in the potentials between the plasma and the collision cell (ΔV_{p-c}) and between the collision cell and the quadrupole (ΔV_{c-q}). Therefore, the variation in V_c changes ion kinetic energy, which affects TaO^+ and HfOH^+ reactivity with O_2 and on the Au^+ signal. Figure 4a shows that as V_c increased toward positive values, Au^+ sensitivity and Au^+/TaO^+ ratio increased markedly under constant V_p (rf power = 1250 W) and V_q (1.0 V). This trend was observed only when V_c was $> V_q$. When $V_c < V_q$, most signals were reduced and defocused because most ions could not overcome the potential barrier between the collision cell and the quadrupole. When $V_c < V_q$ (1.0 V), the energy of the ions in the cell was insufficient to propel the ions into the mass analyzer. When $V_c > V_q$ (1.0 V), no potential barrier existed between the collision cell and the quadrupole; thus, most ions were transmitted into the quadrupole, and the Au^+ signal increased sharply. When $V_c > 7.5 \text{ V}$, Au^+ intensities decreased because ΔV_{p-c} decreased too much. Figure 4b shows the variation in TaO^+/Ta^+ and $\text{TaO}_2^+/\text{TaO}^+$ with V_c . In this case, an increasing V_c indicates a decreasing ΔV_{p-c} . Oxide formation might depend strongly on ΔV_{p-c} , and reactivity increased at high V_c . That is, IKEE had a significant influence on reactivity with O_2 . As V_c increased relative to V_p , the average kinetic energy of the ions decreased, and reaction with O_2 in the cell accelerated. Thus, TaO^+/Ta^+ and $\text{TaO}_2^+/\text{TaO}^+$ ratios increased. This can be explained by the fact that Ta^+ transformed into TaO^+ , which subsequently transformed into TaO_2^+ . TaO^+/Ta^+ decreased at $V_c > 4 \text{ V}$ because most TaO^+ ions transformed into TaO_2^+ due to high reactivity. Although the Au signal decreased when V_c was $> 7.5 \text{ V}$, the Au^+/TaO^+ ratio increased continuously (Figure 4a). This result is due to the same reason discussed above.

These trends were independent of O_2 flow rate. The O_2 flow rate influenced V_c but not the signal intensity or reaction degree.

Influence of Hot Plasma on Cell Bias Voltage (V_c)

The ionization efficiency of Au in ICP is only 51% [27]. Therefore, Au intensity is lower than that of other elements at the same concentration. The result shown in Figure 4c was obtained in hot plasma using a shield torch. Polyatomic ions as well as analyte ions produced in argon plasma are enhanced to a greater extent in hot plasma than in normal plasma. As shown in Figure 4c, hot plasma enhanced Au^+ and TaO^+ intensities, but changed the V_c values with the highest intensities to the lower values. Furthermore, the peak

Figure 4. (a) Influence of hexapole cell bias voltage on Au^+ (open) and Au^+/TaO^+ (closed) ratios for introduction of 1 ng g^{-1} Au and 50 ng g^{-1} Ta solution under two conditions: $0.25 \text{ mL min}^{-1} \text{ O}_2$ (circle) and $0.4 \text{ mL min}^{-1} \text{ O}_2$ (square). (b) Influence of cell bias voltages on TaO^+/Ta^+ (open) and $\text{TaO}_2^+/\text{TaO}^+$ (closed) ratios for introduction of 10 ng g^{-1} Ta solution under two conditions: $0.25 \text{ mL min}^{-1} \text{ O}_2$ (circle) and $0.4 \text{ mL min}^{-1} \text{ O}_2$ (square). (c) Influence of cell bias voltages on Au^+ (open) and Au^+/TaO^+ (closed) ratios for the introduction of 1 ng g^{-1} Au and 10 ng g^{-1} Ta solutions under the conditions of hot plasma combined with a shield torch, rf power = 1250 W , quadrupole bias voltage = -2.0 V , and O_2 flow rate = 0.4 mL min^{-1}

of Au^+/TaO^+ ratio, which was FOUR times greater than the maximum value in normal plasma (Figure 4a), was found at $V_c=9 \text{ V}$.

ΔV_{p-c} can be lowered by decreasing V_p or increasing V_c . In this study, the maximum Au^+ intensity was achieved at $V_c=7.5 \text{ V}$ in normal plasma and at $V_c=4.5 \text{ V}$ in hot plasma. Also, the optimum V_q value shifted from 1.0 to -2.0 V . Therefore, lower V_p in hot plasma shifted the V_c and V_q with the highest intensity to lower values. Since the V_c could be controlled between -10 V and 10 V in our instrument, the peak of Au^+/TaO^+ ratio could not be observed in normal plasma (Figure 4a). On the other hand, when the hot plasma was used, the peak of the ratio was found at $V_c=9$ due to the lowered V_p . It was not obvious whether IKEE was promoted or not in hot plasma than in normal plasma. However, if the maxima of both intensity and ratio in hot plasma were assumed to be found at 3 V lowered V_c than in normal plasma, Au^+/TaO^+ ratio at $V_c=10 \text{ V}$ in normal plasma (Figure 4a) was applicable to that at $V_c=7 \text{ V}$ in hot plasma (Figure 4c). Since two values for the ratio were just similar to each other and about 25, it might be suggested that hot plasma enhanced the intensity and changed the V_c with the highest intensity, but did not promote the IKEE than normal plasma. Although the maximum Au^+/TaO^+ ratio was found at $V_c=9 \text{ V}$, the optimum V_c was chosen as $V_c=5.5 \text{ V}$ because Au^+ intensity was too low at $V_c=9 \text{ V}$ ($<1000 \text{ cps}$ in 1 ng g^{-1} Au solution).

Quadrupole Bias Voltage

The influence of quadrupole bias voltage on Au^+ and Au^+/TaO^+ ratios was investigated at a constant V_c of $+9.9 \text{ V}$. Variation in V_q influenced reactivity in the cell. Figure 5 shows the Au^+/TaO^+ ratios and Au^+ sensitivity as a function of V_q . With $V_q > 6 \text{ V}$, ions, including Au^+ and polyatomic ions, were not able to overcome the energy barrier between

the quadrupole and the collision cell; thus, all signals decreased to background level. Au^+ sensitivity and TaO^+ reactivity with O_2 were unaffected at $V_q < 6 \text{ V}$. Therefore, analyte sensitivity was optimized at $V_q < V_c$.

Influence of He Collision Gas on Optimized Analysis of Au in Real Samples

Instrument optimization for maximum Au^+ signal and minimum TaO^+ ions was necessary to measure Au in a real sample using collision cell ICP-MS. Although hot plasma is effective for achieving a high Au^+ signal under optimized

Figure 5. Influence of quadrupole bias voltage on Au^+ (open) and Au^+/TaO^+ ratios (closed) for the introduction of 1 ng g^{-1} Au and 50 ng g^{-1} Ta solutions under two conditions: $0.25 \text{ mL min}^{-1} \text{ O}_2$ (circle) and $0.4 \text{ mL min}^{-1} \text{ O}_2$ (square). Cell bias voltage = 9.9 V in normal plasma and rf power = 1250 W

Figure 6. Influence of He flow rate on Au^+ , Ta^+ , and Ta oxide species for the introduction of 1 ng g^{-1} Au and 10 ng g^{-1} Ta solutions under conditions of hot plasma combined with a shield torch, rf power = 1250 W, cell bias voltage = 5.5 V, quadrupole bias voltage = -2.0 V , and O_2 flow rate = 0.4 mL min^{-1}

conditions, some TaO^+ ions were not removed and remained unreacted. Residual TaO^+ ions were removed by collision with He gas (Figure 6). Collision gas plays an important role in removing residual TaO^+ ions after reaction with O_2 gas. Although O_2 gas can play a role of collision gas as well as a reaction gas, it can reduce Au^+ and TaO^+ too much before complete removal of polyatomic interferences because it is a large-sized molecule. In the other hand, a smaller collision gas such as He can collide more efficiently with larger polyatomic ions such as TaO^+ than with smaller ions such as monoatomic Au^+ . He collision gas not only enhanced the Au^+ signal but also effectively removed TaO^+ ions in the hot plasma with a shield torch. As shown in Figure 6, TaO^+ ions were

Table 2. Measured concentration of Au spiked in 10 ng g^{-1} Ta and Hf mixed solutions using collision cell QICP-MS under conditions of hot plasma combined with a shield torch, O_2 flow rate = 0.4 mL min^{-1} , He flow rate = 0.66 mL min^{-1} , cell bias voltage = 5.5 V, and quadrupole bias voltage = -2.0 V

Sample No.	Spiked Concentration $C_{\text{spiked}}, \text{pg g}^{-1}$	Observed Concentration $C_{\text{observed}}, \text{pg g}^{-1}$	$C_{\text{observed}}/C_{\text{spiked}}$
1	4.72	6.29 ± 3.57	1.33
2	9.91	14.0 ± 2.4	1.41
3	14.8	20.0 ± 2.7	1.32
4	19.0	18.6 ± 2.9	0.98
5	38.4	37.9 ± 3.6	0.99
6	76.2	80.5 ± 5.7	1.05
7	756	670 ± 30	0.89

Table 3. Mean concentrations and standard deviations (1σ) of Au in mixed reference materials (STM-1 and DGPM-1) using collision cell QICP-MS under conditions of hot plasma using a shield torch, O_2 flow rate = 0.4 mL min^{-1} , He flow rate = 0.66 mL min^{-1} , cell bias voltage = 5.5 V, and quadrupole bias voltage = -2.0 V

STM- : DGPM-1	Observed conc. of Au, $C_{\text{observed}}, \text{ng g}^{-1}$	Specified conc. (ng g^{-1})			$C_{\text{observed}}/C_{\text{spec.}}$
		Au	Hf	Ta	
1 : 1	0.437 ± 0.006	0.398	13.8	9.36	1.10
	0.530 ± 0.005	0.409	13.8	9.36	1.29
	0.593 ± 0.015	0.491	13.9	9.46	1.21
1 : 2	0.504 ± 0.008	0.477	8.35	5.67	1.06
	0.436 ± 0.011	0.426	8.53	5.79	1.02
	0.317 ± 0.003	0.400	8.30	5.63	0.79
1 : 3	0.537 ± 0.012	0.529	6.98	4.73	1.02
	0.471 ± 0.009	0.536	6.91	4.69	0.88
	0.487 ± 0.021	0.532	6.88	4.67	0.92
1 : 4	0.513 ± 0.005	0.562	5.55	3.76	0.91
	0.489 ± 0.015	0.577	5.56	3.77	0.85
	0.487 ± 0.009	0.588	5.55	3.76	0.83
1 : 5	0.397 ± 0.005	0.513	4.16	2.82	0.77
	0.505 ± 0.011	0.563	4.27	2.89	0.90
	0.410 ± 0.008	0.509	4.18	2.84	0.81

removed to background level at He flow rates above 0.6 mL min^{-1} , and the Au^+ signal remained high.

Sample Analysis

Analysis of Spiked Samples

Table 2 shows the analysis results of Au spiked in mixed solutions of 10 ng g^{-1} Ta and Hf. Good agreement between spiked and measured Au concentrations was obtained in solutions with Au concentrations higher than 15 pg g^{-1} Au. The recovery of Au in spiked samples ranged from 89% to 106% (mean values for three measurements). For real samples with Au concentrations $< 15 \text{ pg g}^{-1}$ Au, recoveries were relatively high and ranged from 133% to 141%.

Analysis of Reference Materials

Table 3 shows the analysis results of Au in mixed reference materials. Measured Au concentrations in mixed samples were similar to the crustal abundance, 3 ng g^{-1} . For each sample, the counting standard deviation was $< 4\%$, and the ratios of the measured values to the specified values ranged from 0.77 to 1.29.

Conclusions

This study demonstrated that the collision cell technique effectively eliminated $^{181}\text{Ta}^{16}\text{O}^+$ and $^{180}\text{Hf}^{16}\text{O}^{16}\text{H}^+$ for Au analysis using quadrupole ICP-MS. Removal was achieved by adding O_2 and He to the collision cell as a reaction gas and a buffer gas, respectively. The strong reactivity of major interfering molecular ions such as $^{181}\text{Ta}^{16}\text{O}^+$ and $^{180}\text{Hf}^{16}\text{O}^{16}\text{H}^+$ towards O_2 enabled the measurement of Au. $^{181}\text{Ta}^{16}\text{O}^+$ and $^{180}\text{Hf}^{16}\text{O}^{16}\text{H}^+$ were very unstable and highly

reactive toward O_2 ; thus, they were easily transformed into $^{181}Ta^{16}O_2^+$ and $^{180}Hf^{16}O_2^+H^+$, respectively. Furthermore, the difference in the probabilities of Au^+ and other interfering molecular ions colliding with He buffer gas enabled selective enhancement of the Au signal. The collision cell technique was very sensitive to the O_2 flow rate and the cell bias. Excess O_2 reaction gas and He buffer gas decreased the Au^+ signal as well as oxide signals; the O_2 flow rate was optimized at 0.40 mL min^{-1} and He at 0.66 mL min^{-1} . Instrumental parameters were optimized when cell bias was greater than the quadrupole bias voltage. Under these conditions, the collision cell quadrupole ICP-MS technique further improved gold analysis without pre-concentration. This study confirms the strong potential of collision cell quadrupole ICP-MS for Au analysis without elemental pre-separation or data correction to account for interfering molecular ions.

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