

## ICP - Mass Spectrometry

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## Measurement of Impurities in High-Purity Copper Concentrate Using the NexION 5000 ICP-MS

deposits are chalcopyrite, bornite, chalcocite and covellite. Pyrite and sometimes pyrrhotite are also present as gangue sulfide minerals in copper sulfide deposits.

High-grade copper (Cu) sulfide concentrates, typically greater than about 25% w/w Cu, are commonly treated via pyrometallurgical routes, while hydrometallurgical routes are typically favored for lower-grade or impurity-bearing concentrates. The processing routes for the treatment of copper concentrates can also be influenced by the presence of minor valuable metals, such as nickel, cobalt, silver, gold, palladium and platinum, as well as deleterious metals, such as arsenic, lead and uranium.

Most of the copper concentrates produced around the world contain some impurities, which can affect the price as copper concentrates containing high levels of impurities are not accepted by some smelters. This can render them unsaleable in some countries, as in the case for the high-arsenic-containing concentrates from the Pacific Rim.

To permit treatment and to maximize the value of a copper concentrate, the levels of impurities in the concentrate need to be reduced below the limits set by the smelters and, in some cases, the authorities in the producing and receiving countries.

### Introduction

The dominant copper-containing minerals in most copper sulfide

In order to measure the lowest possible levels of impurities, ICP-MS is required, as it is capable of accurate measurements in the parts per trillion (ppt) range. However, to achieve these levels, both polyatomic and doubly charged interferences must be dealt with. These interferences originate from the plasma and the sample itself.

In this work, we describe the challenges encountered in analyzing impurities in metallurgical concentrate, accuracy and precision comparisons for external calibration versus method of standard addition (MSA) and document the importance of reaction management when using reactive gases, specifically ammonia in this application. This work builds on previous work done using an ICP-MS with a single analyzer quadrupole running in Reaction mode.<sup>1</sup>

## Experimental

### Standard and Sample Preparation

Two samples of copper sulfate at a concentration of 100 g/L were analyzed. Samples were diluted 200x with ultrapure water (UPW) prior to analysis and acidified to 1% nitric acid. The samples were analyzed for the following elements: Ag, Al, As, Au, Bi, Cd, Co, Cr, Fe, Ir, Mg, Mn, Na, Ni, P, Pb, Pd, Pt, Rh, Ru, Se, Sb, Si, Te and Zn.

Samples were measured both by external calibration using yttrium and terbium as internal standards and with the method of standard addition (MSA) for comparison.

An external blank and calibration standards were prepared in 1% nitric acid (v/v) at concentrations of 1, 2, 3 and 5 ppb for the minor elements and 100, 200, 300 and 500 ppb for P and Si. Internal standards, also in 1% nitric acid, were added via the High Throughput System (HTS) sample introduction module (PerkinElmer Inc., Shelton, Connecticut, USA), ensuring optimal mixing prior to analysis.

Both samples were analyzed by MSA, adding 1, 2 and 3 ppb for the minor elements and 100, 200 and 300 ppb for P and Si, respectively to each sample.

### Instrumentation

PerkinElmer's NexION® 5000 Multi-Quadrupole ICP-MS, described in detail in the NexION 5000 product note, represents a truly significant advancement in ICP mass spectrometry and in the removal of spectral interferences in elemental analyses.<sup>2</sup> Therefore, it is perfectly suited for analysis of trace elements in pure copper concentrate.

For this analysis, the NexION 5000 was used in a variety of different modes. The OmniRing™ and hyper-skimmer cone of the second-generation Triple Cone Interface were set to Extraction or Focusing modes, depending upon the element of interest. Three different scan types were used to obtain the best results for the different analytes: Single Quad (known as Q1 or Q3 only), MS/MS and Mass Shift; the latter two modes were used with different reaction gases in the Universal Cell. The scan types and cell gases for each element can be seen in Table 1.

Table 1. Potential interferences, modes and gases used for analysis of Cu concentrate samples.

Element	Possible Interference	Scan Type	Cell Gas	Q1 (amu)	Q3 (amu)
Ag		Q3			109
Al	N <sub>2</sub> spread	MS/MS	Ammonia	27	27
As	<sup>40</sup> Ar <sup>35</sup> Cl, <sup>59</sup> Co <sup>16</sup> O <sup>+</sup> , <sup>12</sup> C <sup>31</sup> P <sup>16</sup> O <sub>2</sub> <sup>+</sup>	Mass Shift	Oxygen	75	91
Au		Q3			197
Bi		MS/MS		209	209
Cd		Q3			111
Co	<sup>24</sup> Mg <sup>35</sup> Cl <sup>+</sup>	MS/MS	Ammonia	59	59
Cr	<sup>40</sup> Ar <sup>12</sup> C <sup>+</sup> <sup>35</sup> Cl <sup>16</sup> OH <sup>+</sup>	MS/MS	Ammonia	52	52
Fe	<sup>40</sup> Ar <sup>16</sup> O <sup>+</sup> , <sup>40</sup> Ca <sup>16</sup> O <sup>+</sup> , <sup>28</sup> Si <sub>2</sub> <sup>+</sup>	MS/MS	Ammonia	56	56
Ir		Q3	Ammonia		193
Mg	<sup>12</sup> C <sub>2</sub> <sup>+</sup>	MS/MS	Ammonia	24	24
Mn	<sup>40</sup> Ar <sup>14</sup> NH	MS/MS	Ammonia	55	55
Na		MS/MS	Ammonia	23	23
Ni	<sup>44</sup> Ca <sup>16</sup> O <sup>+</sup> , <sup>43</sup> Ca <sup>16</sup> OH <sup>+</sup> , <sup>44</sup> Ca <sup>16</sup> O <sup>+</sup> , <sup>23</sup> Na <sup>37</sup> Cl <sup>+</sup> , <sup>25</sup> Mg <sup>35</sup> Cl <sup>+</sup>	MS/MS	Oxygen	60	60
P	<sup>63</sup> Cu <sup>+</sup> , <sup>14</sup> N <sup>16</sup> OH <sup>+</sup>	Mass Shift		31	47
Pb	<sup>190</sup> Pt <sup>16</sup> O <sup>+</sup>	Q3			208
Pd	<sup>40</sup> Ar <sup>65</sup> Cu <sup>+</sup> , <sup>36</sup> Ar <sub>2</sub> <sup>16</sup> O <sup>17</sup> O <sup>+</sup>	Q3			106
Pt		Q3	Ammonia		195
Rh	<sup>40</sup> Ar <sup>63</sup> Cu <sup>+</sup>	MS/MS	Ammonia	103	103
Ru	<sup>36</sup> Ar <sup>63</sup> Cu <sup>+</sup>	MS/MS	Ammonia	104	104
Sb	<sup>61</sup> Ni <sup>37</sup> Cl <sup>+</sup>	MS/MS	Oxygen	121	121
Se	<sup>40</sup> Ar <sup>38</sup> Ar <sup>+</sup> , <sup>63</sup> Cu <sup>17</sup> O <sup>+</sup> , <sup>65</sup> Cu <sup>170</sup> +, <sup>62</sup> Ni <sup>16</sup> O <sup>+</sup> , <sup>46</sup> Ca <sup>16</sup> O <sub>2</sub> <sup>+</sup>	Mass Shift	Ammonia	78	94
Si	<sup>14</sup> N <sub>2</sub> <sup>+</sup> , <sup>12</sup> C <sup>16</sup> O <sup>+</sup>	MS/MS		28	28
Te		MS/MS	Ammonia	130	130
Zn	<sup>40</sup> Ar <sup>14</sup> N <sub>2</sub> <sup>+</sup> , <sup>40</sup> Ar <sup>12</sup> C <sup>16</sup> O <sup>+</sup> , <sup>63</sup> CuH <sup>3+</sup> , <sup>52</sup> Cr <sup>16</sup> O <sup>+</sup>	MS/MS		68	68

The NexION 5000 ICP-MS was configured with a PerkinElmer HTS system and an S23 autosampler, used for the automated sample introduction (PerkinElmer Inc.). The conditions of the NexION 5000 and HTS system are shown in Table 2.

Table 2. Conditions used for the analysis of Cu concentrate samples.

	Parameter	Value
NexION 5000 ICP-MS	Plasma gas flow (L/min)	16
	Aux flow (L/min)	1.2
	RF power (W)	1600
	Neb gas flow (L/min)	1.04
	Spray chamber temperature	5 °C
	Pump tubing - Carrier	Yellow/Green
	Pump tubing - IS	Green/Orange
	Sample flow rate	145 µL/min
HTS High Throughput Introduction System	Loop size	2 mL

## Results and Discussion

The high Cu matrix has the potential for creating new interferences. Some of these would be formed in the plasma, while others have the potential to be formed in the cell with the reaction gas that is being used. Table 1 shows the potential interferences and which analytes may be affected.

Interferences formed within the cell from “off-mass” ions are only a potential issue for single-quadrupole ICP-MS as well as triple- or multi-quadrupole ICP-MS systems that are being run in Single Quad mode, where the first quadrupole (Q1) transfers all ions into the cell. The unique properties of a quadrupole reaction cell, however, offer certain benefits over passive cells in this regard. For example, in Single Quad mode in a high Cu matrix, Cu can react with ammonia to form a  $\text{Cu}(\text{NH}_3)^+$  complex. This complex has a mass of 80 amu and can interfere with  $^{80}\text{Se}$ . However, in a quadrupole cell, such as the NexION 5000's Universal Cell, a rejection parameter can be applied to the cell to control this side reaction. Triple- and multi-quadrupole ICP-MS systems being run in MS/MS mode do not suffer from this type of interference as the first quadrupole (Q1) will be set to 80 amu, preventing the Cu ions from entering the Universal Cell and forming  $\text{Cu}(\text{NH}_3)^+$ .

However, in cases where the interference is formed in the plasma and already has the same mass as the analyte of interest in a triple- or multi-quadrupole system, both the interferent and analyte will pass through Q1 and into the cell. Collision or Reaction modes will then be used to remove the interference or mass shift the analyte to a different mass. But there is the potential for unwanted side reactions to take place and new interferences to form from the reaction gases and impurities in the reaction gas.<sup>3</sup> Here, the rejection parameter of the quadrupole Universal Cell is applied to prevent new interferences from forming in the cell. In this way, the NexION 5000 Multi-Quadrupole ICP-MS is not only able to control the ions which enter the cell but also control the reaction within the cell.

### $^{63/65}\text{Cu}^{40}\text{Ar}^+$ Interference on $^{103}\text{Rh}^+$

A mechanism for the removal of the  $^{63}\text{Cu}^{40}\text{Ar}^+$  interference on  $^{103}\text{Rh}^+$  is discussed in detail here; similar approaches were used to remove ammonia-based interferences on other analytes, as shown in Table 2.

Figure 1a shows a spectrum of a pure Cu (1 ppm) solution. The first analyzer quadrupole (Q1) was set to allow all masses, while the Universal Cell was in Standard mode and the second analyzer quadrupole (Q3) was set to scan masses 81-110 amu. In this mass range,  $^{65}\text{Cu}^{16}\text{O}^+$  at mass 81 can be seen along with the two  $^{63/65}\text{Cu}^{40}\text{Ar}^+$  peaks at 103 and 105 amu respectively. Both  $\text{CuO}^+$  and  $\text{CuAr}^+$  are formed in the plasma.

While aspirating a pure Cu solution, the ion beam can be cleaned up by setting Q1 to transmit only mass 103. Scanning the mass range from 81 to 110 amu on Q3 in Standard mode reveals just the  $^{63}\text{Cu}^{40}\text{Ar}^{63}$  peak at mass 103 (Figure 1b). This would give a false positive result for Rh. To remove the  $^{63}\text{Cu}^{40}\text{Ar}^+$  interference on Rh, a reaction gas that does not affect  $\text{Rh}^+$  but removes  $\text{CuAr}^+$  interference has to be used in the cell.

Pure ammonia (at 100%) is an ideal reaction gas to remove the  $\text{CuAr}^+$  interference on Rh due to its fast reaction with  $\text{CuAr}^+$  and slow reaction with  $\text{Rh}^+$  (rate constant  $\approx 10^{-12}$ ).

Finally, the pure Cu solution was spiked with Rh (Figure 1D). Q1 was set to 103, the reaction with ammonia occurred in Q2, and Q3 was scanned between 81 and 110 amu. In this case, as shown in Figure 1c, ammonia creates a cluster with Cu at mass 97 and Rh can easily be resolved and analyzed free from interferences at mass 103 when run in MS/MS mode.

### MDLs, Results and Spike Recoveries

The method detection limits (MDLs) can be seen in Figure 2. They were determined by measuring seven blanks of 1% nitric acid (using the external calibration) and their standard deviations multiplied by 3.14 and the dilution factor.

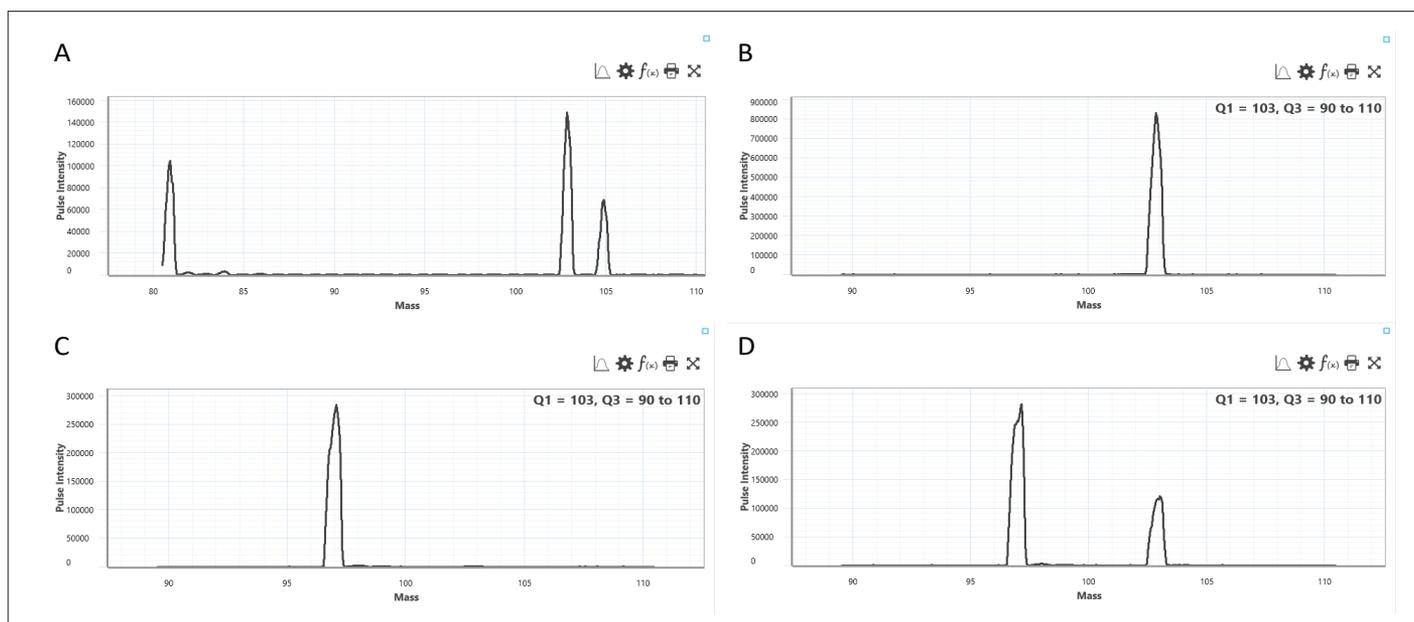


Figure 1. Mechanism of removing spectral interferences on Rh: (a) Product Ion scan of 1 ppm Cu solution in Q3 only mode; (b) Product Ion scan of 1 ppm Cu solution in MS/MS mode; (c) Product Ion scan of 1 ppm Cu solution in MS/MS mode with  $\text{NH}_3$  as a reaction gas; (d) Product Ion scan of 1 ppm Cu and 1 ppb Rh solution in MS/MS with  $\text{NH}_3$  as a reaction gas.

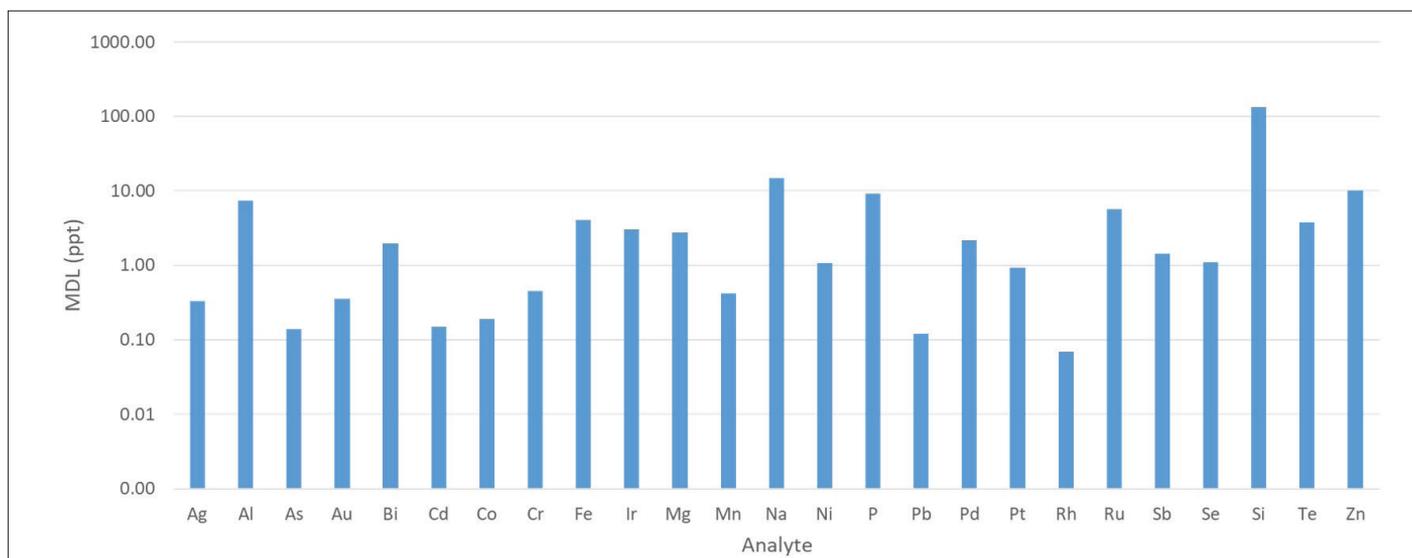


Figure 2. MDLs determined in 1% nitric acid using the scan types indicated in Table 1.

Two Cu concentrate samples were analyzed five times using both the external and MSA calibrations. The values seen in Table 3 are the average of these five results. Both samples show good correlation between results obtained with the external calibration and MSA, demonstrating that external calibrations can be used for these types of analyses to provide accurate results.

Table 3. Impurity concentrations for Samples 1 and 2 obtained with the external and MSA calibrations.

Element	Sample 1 Ext (ppb)	Sample 1 MSA (ppb)	Variation (%)	Sample 2 Ext (ppb)	Sample 2 MSA (ppb)	Variation (%)
Ag	77.99	79.97	3	173.24	185.04	7
Al	<DL	<DL	N/A	<DL	<DL	N/A
As	<DL	<DL	N/A	<DL	<DL	N/A
Au	<DL	<DL	N/A	<DL	<DL	N/A
Bi	<DL	<DL	N/A	<DL	<DL	N/A
Cd	<DL	<DL	N/A	<DL	<DL	N/A
Co	25.73	24.9	3	26.47	26.88	2
Cr	4.51	4.62	2	<DL	<DL	N/A
Fe	36.14	36.56	1	19.95	21.36	7
Ir	<DL	<DL	N/A	<DL	<DL	N/A
Mg	<DL	<DL	N/A	<DL	<DL	N/A
Mn	<DL	<DL	N/A	<DL	<DL	N/A
Na	<DL	<DL	N/A	<DL	<DL	N/A
Ni	87.36	89.11	2	107.24	109.53	2
P	<DL	<DL	N/A	<DL	<DL	N/A
Pb	15.04	14.84	1	74.76	78.35	5
Pd	<DL	<DL	N/A	<DL	<DL	N/A
Pt	10.72	10.86	1	20.74	22.41	8
Rh	<DL	<DL	N/A	<DL	<DL	N/A
Ru	<DL	<DL	N/A	<DL	<DL	N/A
Sb	<DL	<DL	N/A	<DL	<DL	N/A
Se	<DL	<DL	N/A	<DL	<DL	N/A
Si	<DL	<DL	N/A	<DL	<DL	N/A
Te	13.94	14.59	5	15.15	14.39	5
Zn	<DL	<DL	N/A	<DL	<DL	N/A

Both copper sulfate samples were spiked with 1 ppb of all elements, with the exception of P and Si where the spike was 100 ppb. Excellent spike recoveries, well within 10% of the specified value, were found for all analytes in both samples (Figure 3).

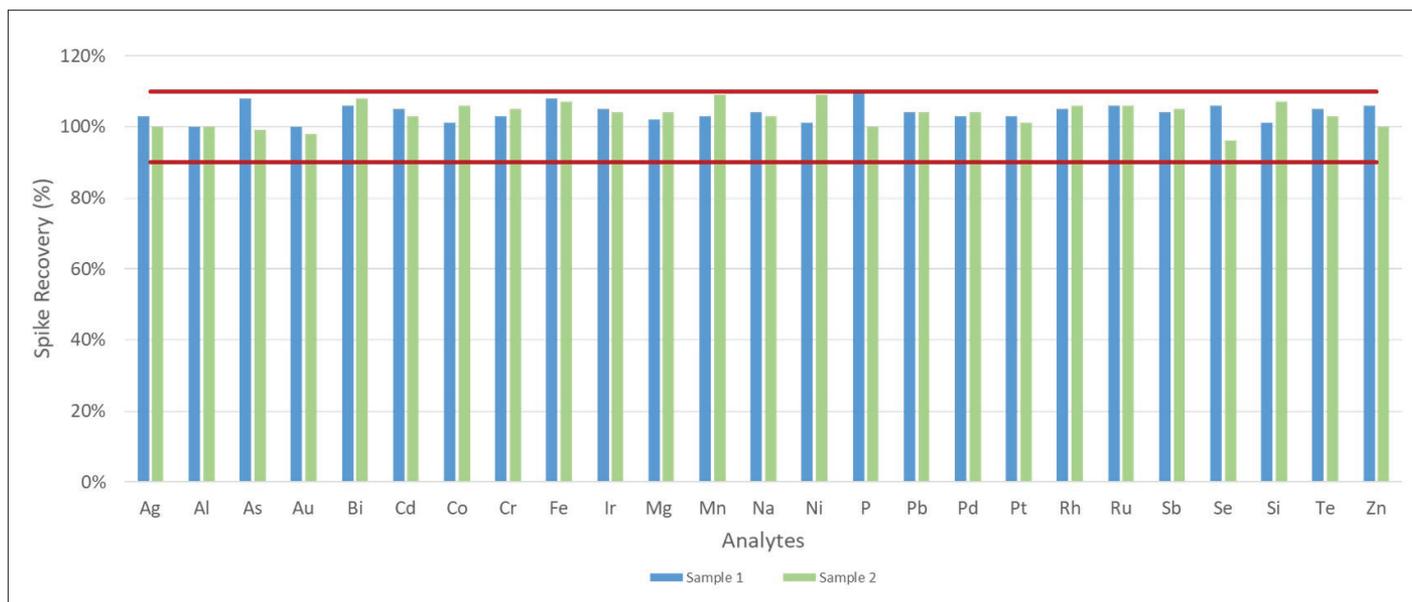


Figure 3. Spike recoveries in Cu concentrate samples.

## Conclusion

This work demonstrates the accurate and reliable quantification of impurities in Cu concentrate samples using the NexION 5000 ICP-MS. Both the external calibration and MSA approaches to the analysis were found to deliver comparable results and are suitable for this sample type.

The unique capabilities of the NexION 5000 Multi-Quadrupole ICP-MS and Universal Cell Technology were proven to be effective at removing spectral interferences, as demonstrated for removal of the CuAr<sup>+</sup> polyatomic interference on Rh<sup>+</sup>. The MDLs obtained permit the determination of extremely low-level impurities in Cu concentrates, whereas excellent spike recoveries demonstrate the accuracy and reliability of the method. Both of these factors are essential in driving process control and increasing the yield and value of the copper end-products.

## References

1. "Geological Analyses with the ELAN DRC II" PerkinElmer Application Note, 2004.
2. "NexION 5000 Multi-Quadrupole ICP-MS" PerkinElmer Product Note, 2020.
3. Kroukamp, E., Abou-Shakra, F., "Multi-Quadrupole ICP-MS: Pushing Limits of Detection to the Next Decimal", Spectroscopy, 2020, 35 (9), 16-22.

## Consumables Used

Component	Part Number
HTS Carrier Peristaltic Pump Tubing, Green/Yellow (0.44 mm id), PVC	N8152404
HTS Internal Standard Peristaltic Pump Tubing, Green/Orange (0.38 mm id), PVC	N8152403
HTS Drain Peristaltic Pump Tubing, Gray/Gray (1.30 mm id), Santoprene	N8152415
17-Element Solution, 5% HNO <sub>3</sub> , 1000 µg/mL, 500 mL	N9307116
10-Element Solution, 10% HCl/1% HNO <sub>3</sub> , 10 µg/mL, 125 mL	N9300234
Silicon (Si) Pure Plus Standard	N9304264