

# Direct Analysis of 13 Trace Elements in Tea Infusions using ICP-MS

Use of an Integrated Sample Introduction System eliminates sample preparation and overcomes common problems of direct analysis



## Authors

Raquel F. Milani, Leandro I. Peron,  
Elisabete S. Saron, Marcelo A. Morgano  
Instituto de Tecnologia de Alimentos,  
Campinas SP, Brasil

Fabio F. Silva  
Agilent Technologies, Brasil, São Paulo,  
SP, Brasil

Solange Cadore  
Universidade Estadual de Campinas,  
Campinas, SP, Brasil

## Introduction

Tea, when prepared by infusion of leaves, flowers, or roots, has generated significant scientific interest due to its antioxidant activity and presence of some beneficial micronutrients, such as minerals, flavonoids, and catechins (1). Studies have also shown the presence of potentially toxic and cumulative substances in herbs such as inorganic or elemental contaminants (2). These contaminants originate from different aspects of the herbal tea manufacturing process and include sources such as soil and water, fertilizers, and airborne industrial emissions (3). Elements may also be introduced during tea processing and from packaging materials, so manufacturers and regulatory bodies need to monitor elemental contaminants in final tea products to ensure consumer safety.

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7850 ICP-MS



One of the most common methods to measure trace element concentrations in tea samples is ICP-MS determination after sample digestion. This method requires a microwave digestion system and involves hazardous reagents such as concentrated acids and oxidizing agents. The whole digestion process can also impose a dilution factor of 10–100 times, compromising detection limits. Conversely, the high matrix levels in sample run by direct analysis of an infusion can also compromise performance parameters, such as precision, long-term stability, matrix deposition, and increased maintenance.

The Integrated Sample Introduction System (ISIS) accessory for Agilent ICP-MS instruments uses a loop injection system for Discrete Sampling (DS). ISIS DS provides the advantage of minimizing sample use, avoiding unnecessary sample exposure by the ICP-MS sample introduction system. In addition, DS mode has the ability to maintain instrument performance and provide high speed analysis when combined with the unique capabilities of ORS<sup>3</sup> and He as collision gas.

The synergy between a collision cell that operates effectively with an inert cell gas (helium) and discrete sampling results in excellent performance as measured by detection limits, precision, and throughput. This application note demonstrates the benefits of discrete sampling to provide an easy-to-use method for the determination of 13 elements in tea infusions. The method is combined with effective control of common polyatomic ion interferences using a single helium cell gas mode.

## Experimental

The Agilent 7700x\* ICP-MS System was used with the standard sample introduction system, which includes a MicroMist glass concentric nebulizer, quartz double pass spray chamber, connector tube with dilution port, a quartz torch with 2.5-mm id injector, and standard nickel cones. The ICP-MS was fitted with an Agilent I-AS autosampler. Discrete Sampling (DS) was performed with the ISIS switching valve. ISIS works with the ICP-MS to deliver only the required amount of sample, achieving productivity gains, and further improving long-term matrix tolerance while reducing run time and sample exposure as much as possible. A preconfigured ISIS tubing kit for ISIS-DS is available for easy setup and convenience.

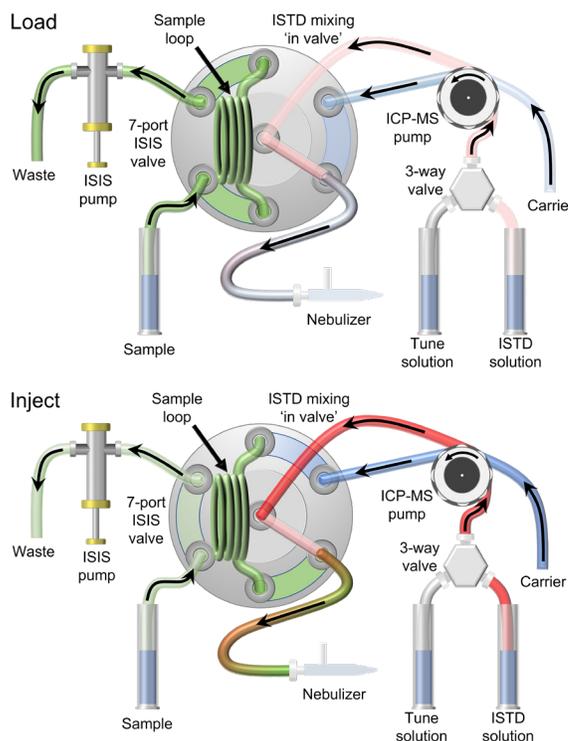
Figure 1 shows a schematic of the ISIS-DS configuration and operation. While there is a continuous flow of the internal standards and carrier solutions, the sample fills the loop when the valve is in the load position. The valve then switches to the inject position, sending the carrier solution through the sample loop and pushing the sample into the nebulizer.

A detailed description of the ISIS-DS operation can be found in previous publications (4, 5).

The ICP-MS tuning was based on a preset method for food applications using ICP-MS MassHunter software. No Gas, He, and HEHe modes were used in this method and the tuning conditions can be found in Table 1.

For calibration, the 13 elements were divided into two groups; one in the lower concentration range (0, 0.1, 0.5, 1, 5, 10, and 100 µg/L) including As, Cd, Cr, Cu, Hg, Ni, Pb, and Se, and the other in the higher concentration range (0, 10, 100, 250, 500, 1,000, and 2,000 µg/L) including Al, Ba, Fe, Mn, and Zn. Both groups of standards were prepared in HNO<sub>3</sub> 0.2% v/v. The method did not require matrix matching or recalibrations. A Sc, Ge, and Y solution containing 250 µg/L of each element was used as online internal standard.

After initial calibration, a sequence with 10 analytical blanks was run to provide standard deviation (s) and calculate detection limits (DL = 3 × s) and quantification limits (QL = 10 × s). Repeatability was calculated using coefficient of variation (CV with n = 16). Due to the lack of certified reference materials for the tea infusion matrix, accuracy was assessed through spike recovery of the analytes. In both cases (precision and accuracy), the infusion samples were spiked at different concentration levels: As, Cd, Cr, Cu, Hg, Ni, Pb, and Se at 10 and 50 µg/L; Al, Ba, Fe, Mn, and Zn at 250 and 500 µg/L.



**Figure 1.** ISIS operation at DS mode: Valve in load position (A) and injection position (B).

**Table 1.** Agilent ICP-MS and ISIS-DS operating conditions.

ICP-MS parameters	
RF power (W)	1,550
Carrier gas flow (L/min)	1.1
Number of elements/internal standards	13/3
Replicate/peak pattern/sweeps	3/3/100
Reading time (s)	60
Cell tuning modes	No Gas/ He/ HEHe
Cell gas stabilization time (s)	5
He cell gas flow rate (mL/min)	7 (10*)
KED bias (V)	5 (7*)
Agilent ISIS-DS parameters	
Loop volume and size (μL/cm)	150/30
Uptake time (s)	20
Acquisition delay (s)	20
Rinse time	Pre-emptive rinse during acquisition

\*Enhanced He mode

Method performance was verified using four varieties of tea as detailed in Table 2. For each variety, the study tested three different brands purchased at a local market (2013 Campinas, SP - Brazil), and for each brand, three infusions were prepared. Infusion preparation was done by boiling 200 mL of deionized water (18.2 MΩ.cm) with 1.5 g of sample (equivalent to a commercial tea bag) for 3 minutes. After cooling, the infusions were acidified (HNO<sub>3</sub> 0.2% v/v) and filtered through a 250 μm polymeric membrane and transferred to the autosampler vials.

**Table 2.** Tea samples used in method application.

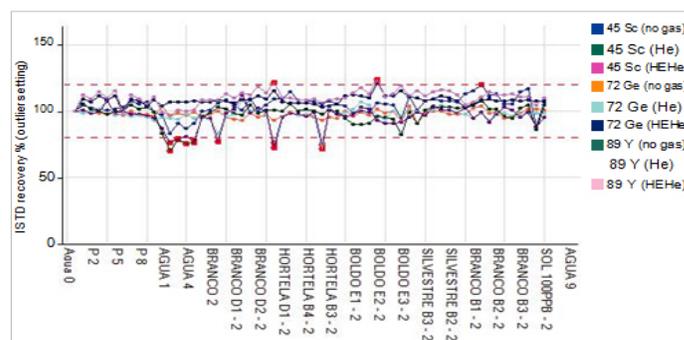
<b>Lemon balm</b>	Leaves of <i>Melissa officinalis</i> , L.
<b>Fennel</b>	Fruits of <i>Pimpinella anisum</i> , L.
<b>Flowers and fruits</b>	Apple Fruit - <i>Pyrus malus</i> L. Flowers Hibiscus - <i>Hibiscus sabdariffa</i> , L. Fruits and Flowers Wild Rose - <i>Rosa canina</i> , L. Orange Peel - <i>Citrus aurantium</i> , L. Lemon Peel - <i>Citrus Limonum</i> , (L.) Osbeck leaves Stevia - <i>Stevia rebaudiana</i> , Bert
<b>Red</b>	Stems and leaves of <i>Camellia sinensis</i> (L.) Kuntze

## Results and discussion

Laboratories that perform routine tea analysis require high throughput, low DLs, and good precision and accuracy. All these figures of merit are discussed below.

### Productivity and stability

In an analysis process, one of the most time-consuming steps is sample preparation. The replacement of conventional digestion by direct sample introduction dramatically reduces the analysis time. Some standard features of the Agilent ICP-MS such as the MicroMist nebulizer, Peltier-cooled double pass spray chamber, High Matrix Introduction (HMI) system, wide diameter (2.5 mm id) torch injector, and solid state RF (27 MHz) generator are important to ensure a robust performance in challenging matrices such as those used in this study. These features result in a very robust plasma with CeO<sup>+</sup>/Ce<sup>+</sup> ratios lower than 1.5%. Even with this robust plasma performance, extended routine analysis of tea samples can cause matrix buildup and internal standard instability. This requires maintenance stops for cleaning or replacement of some sample introduction parts. With ISIS-DS, it is possible to overcome these problems by reducing ICP-MS sample exposure by 3 to 4 times, resulting in increased overall system stability. The good system stability is indicated by the 2-hour internal standard signals shown in Figure 2.



**Figure 2.** Internal standard recoveries normalized to the calibration blank for all samples.

Comparing total analysis time per sample (sample uptake, stabilization, reading, and rinse times), DS-ICP-MS achieved 30% faster analysis compared to conventional ICP-MS (from 197 seconds to 136 seconds). This analysis time reduction was achieved by DS mode only. The ORS<sup>3</sup> contribution is also significant, because all common polyatomic interferences can be addressed using just He mode (standard and HEHe modes). Also the small internal volume of the cell allows the cell gas mode to be switched in approximately 5 seconds. The analyst can then choose more than one cell mode in the same method with no significant increase in analysis time.

Regarding food quality control, some contaminant elements can be harmful such as Al, As, Ba, Cd, Hg, Ni, and Pb. Other elements are essential nutrients, such as Fe, Mn, and Zn, while others, such as Cu, Cr, and Se can be both harmful and essential, depending on the level. Usually, harmful contaminants are present at low levels in a sample, while nutrients can be present at higher levels. This is a challenge faced by food analysts, because it is difficult to combine different concentration ranges in a single method or even in a single instrument. The Agilent ICP-MS dual stage detector can obtain calibration curves for all these elements in different ranges with linearity ( $R^2$ ) greater than 0.9999.

### Detection limits, precision, and recovery

Direct analysis of tea samples minimized sample handling, thereby decreasing the risk of contamination and the need to store, handle, and dispose of hazardous chemicals. In addition, this method does not require dilution, thereby improving detection limits. The fast switch between cell modes provides the opportunity for the user to analyze with the optimum cell mode for each analyte. For example, <sup>52</sup>Cr<sup>+</sup> has a strong interference from <sup>12</sup>C<sup>40</sup>Ar<sup>+</sup>, but in this application Cr could be easily quantified in He mode. <sup>202</sup>Hg<sup>+</sup>, which has no polyatomic interference observed in tea infusion analysis, could be analyzed in No Gas mode. The effective He mode performance reduces background spectral overlaps and lowers detection limits. Another factor in lowering detection limits is the potential for contamination in standard laboratory environments. Sample contamination commonly affects elements such as Al, Cu, Mn, and Zn. Table 3 lists DLs, QLs, and other performance measures as well as the best analysis conditions for the analytes studied.

Using the conditions proposed by this method, it was possible to keep the precision values less than 20%, and recoveries in the two levels between 82 and 121%.

**Table 3.** Analysis conditions and performance measures.

Isotope	Cell mode	Detection limit (µg/L) (3s)	Quantification limit (µg/L) (10s)	Precision (%)	Recovery (%)	
					Level 1	Level 2
<sup>27</sup> Al	He	6	20	13	103 ± 5	99 ± 3
<sup>52</sup> Cr	He	0.09	0.29	17	85 ± 1	91 ± 1
<sup>55</sup> Mn	He	0.11	0.38	11	87 ± 4	89 ± 6
<sup>56</sup> Fe	HEHe	0.66	2.2	8	85 ± 4	92 ± 3
<sup>60</sup> Ni	He	0.63	2.1	10	82 ± 1	89 ± 1
<sup>63</sup> Cu	-	0.51	1.7	2	95 ± 5	92 ± 1
<sup>66</sup> Zn	He	10	35	15	95 ± 6	95 ± 3
<sup>75</sup> As	HEHe	0.14	0.46	4	96 ± 2	104 ± 2
<sup>80</sup> Se	HEHe	0.15	0.50	3	106 ± 2	110.5 ± 0.4
<sup>111</sup> Cd	-	0.016	0.053	4	99 ± 1	100 ± 1
<sup>138</sup> Ba	He	0.60	2.0	12	110 ± 8	111 ± 3
<sup>202</sup> Hg	-	0.10	0.34	9	111 ± 4	121.0 ± 0.4
<sup>206</sup> Pb	HEHe	0.12	0.39	6	112 ± 3	113 ± 2

### Sample analysis

After optimizing analysis conditions and evaluating the method performance, three samples of four selected varieties of tea were analyzed in triplicate to verify the performance of the method while running real samples. Table 4 shows the results.

The data show the method capability, using the discrete sampling system ISIS-DS, for quantifying extremely low concentrations of several elements, including those that are considered potentially harmful (such as As, Cd, Cr, Hg, and Pb).

Results showed a large variation in concentration values when comparing different varieties of tea infusions. It was determined that the infusion of red tea had the highest concentrations of Al, As, Cr, Mn, Ni, and Pb. However, no sample presented values higher than the maximum established in Resolution 12/11 where the stated limits are: 600 µg As/L, 600 µg Pb/L, and 400 µg Cd/L (7).

**Table 4.** Average result and concentration range of the tea infusions analyzed.

Element	Average result and range (n = 3, µg/L)			
	Lemon balm	Fennel	Flowers and fruits	Red
Al	ND < 20	32 (31–34)	28 (24–32)	954 (882–1,033)
As	ND < 0.46	ND < 0.46	0.18 (ND < 0.46–0.53)	0.76 (ND < 0.46–1.8)
Ba	16 (8.2–21)	7.7 (7.0–8.1)	103 (89–111)	15 (13 - 20)
Cd	0.093 (ND < 0.053–0.21)	ND < 0.053	0.021 (ND < 0.053–0.063)	ND < 0.053
Cr	ND < 0.29	ND < 0.29	0.33 (ND < 0.29–0.53)	0.66 (0.58–0.74)
Cu	7.7 (5.2–9.2)	21 (19–22)	9.8 (6.1–13)	6.3 (4.5–9.7)
Fe	18 (11–24)	53 (27–70)	91 (70–102)	65 (47–81)
Hg	ND < 0.34	ND < 0.34	ND < 0.34	ND < 0.34
Mn	509 (157–896)	56 (47–62)	405 (357–434)	1020 (951–1,131)
Ni	ND < 2.1	ND < 2.1	3.2 (2.1–4.5)	19 (16–22)
Pb	0.43 (ND < 0.39–0.86)	ND < 0.39	0.22 (ND < 0.39–0.65)	0.78 (ND < 0.39–1.3)
Se	ND < 0.50	ND < 0.50	ND < 0.50	ND < 0.50
Zn	21 (ND < 35–62)	42 (37–46)	ND < 35	30 (ND < 35 - 45)

\*ND = Non Detected

## Conclusion

This application note describes the development and validation of an analytical methodology for the determination of the total concentration of 13 elemental contaminants and micronutrients in tea infusions using a direct analysis approach with ISIS-DS. This method provides significant benefits in terms of reduced cycle time and sample handling. Trace amounts for all 13 chemicals were found to be below published regulatory limits (7).

This method can be used to monitor tea infusions with good precision and accuracy and can also be adapted for other drinks such as coffee and fruit juices.

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