

Application Note # CA-270105

Direct Determination of Trace Elements in Urine using the Bruker 820-MS

Introduction

Inductively Coupled Plasma Mass Spectrometry offers low detection limits, multi-element capabilities, simplified sample preparation and low sample consumption. It is very useful for the determination of trace and ultra-trace elements in various biological samples.

The Bruker 820-MS is equipped with Bruker's patented 90 degree ion mirror ion optics [1] and Collision Reaction Interface (CRI) [2]. The 90 degree ion optics offers unsurpassed efficiency of transfer of ions from the interface to the mass analyzer [3], and enables the Bruker 820-MS to achieve a sensitivity of over 1000 million c/s per mg/L of an isotope in solution without compromising oxide and/or doubly-charged interference performance. Bruker's CRI technology reduces common polyatomic interferences on elements such as As, Se, Cr, V and Fe, thus achieving lower detection limits in hot plasma, even for samples with complex matrices.

This work demonstrates the capability of the Bruker 820-MS for direct trace metal determinations in complex matrices such as urine samples.

Instrumentation

Direct multi-element analysis of urine control materials was carried out using a Bruker 820-MS. All the work was done under routine analytical laboratory and not 'clean room' conditions. Bruker ICP-MS Expert software is used to control the instrument, including setup and automatic optimization. Typical method parameters (including the CRI settings) used for the urine analyses are listed in Table 1.

	Instrument Parameters	Settings
Gas Flow Parameters (L/min)	Plasma flow	16.5
	Auxiliary flow	1.65
	Nebulizer flow	0.95
	Sheath flow	0.25
Plasma Power	RF power (kW)	1.38
Sample Introduction	Sampling depth (mm)	7.5
	Pump rate (rpm)	3
Ion Optics (v)	First extraction lens	-5
	Second extraction lens	-135
	Third extraction lens	-238
	Corner lens	-198
	Mirror lens left	35
	Mirror lens right	35
	Mirror lens bottom	35
	Fringe bias	-3.8
CRI Gas Settings	Skimmer gas source	He
	Skimmer flow (mL/min)	130
Quadrupole Scan	Scan mode	Peak Hopping
	Dwell time (ms)	20
	Points per peak	1
	Scans/Replicated	25
	Replicates/Sample	5

Table 1. Typical key method settings for the urine analysis

Materials and reagents

High purity nitric acid and hydrochloric acid (both AR Select® Plus, Mallinckrodt Baker, Phillipsburg, NJ, USA), iso-propanol (IPA) (SupraSolv® 2-propanol for gas chromatography, Merck KGaA, Darmstadt, Germany) and deionized water (18 MΩ cm, Millipore Milli-Q, Billerica, MA, USA) were used in the preparation of sample and calibration solutions. All labware, new or used, was thoroughly cleaned by acid washing and rinsing, and then the clean containers were left filled with 2% v/v HNO₃ until use. Three multi-element calibration solutions were prepared, at concentration levels of 1 µg/L, 5 µg/L, and 10 µg/L, by

diluting a 10 mg/L multi-element standard stock (SPEX CertiPrep, Inc., Metuchen, NJ, USA) with 2% v/v HNO₃. An internal standard solution, containing 20 µg/L of ⁶Li, ⁴⁵Sc, ¹¹⁵In, ⁸⁹Y, ¹⁵⁹Tb and ²⁰⁹Bi, was prepared by diluting a 100 mg/L internal standard stock (Var-IS-1, Inorganic Ventures, Inc., Lakewood, NJ, USA) with 2% v/v HNO₃. The internal standard was added to the nebulizer through a 'Y-piece' using the third channel of the Bruker 820-MS sampling pump.

Quality control materials (such as standard or certified reference materials) are commonly used in many routine analytical laboratories to ensure the accuracy of the instrument and the analytical procedure/method. In this work, two urine metals control materials (Lyphochek® Urine Metals Control, Level-1 (LOT 69101) and Level-2 (LOT 69102), Bio-Rad Laboratories, Irvine, CA, USA) were selected as the sample for the direct trace element determination using the Bruker 820-MS.

Results and discussion

Interference reduction with the Bruker CRI:

As described in a previous application note [4], the CRI works by injecting reactive/collision gas (H₂ and/or He) into the plasma through the tips of the sampler and/or skimmer cones, to induce collisions, electron-ion reactions or ion-molecule interactions with interfering ions within the plasma. As a result, most argon-based polyatomic interferences are destroyed or removed before the ions are extracted into the ion optics.

CRI experimental results obtained so far have indicated that gas injected at the skimmer cone has greater effect on interference reduction. Figure 1 shows typical results of interference reductions in three-dimensional graphs, where the sensitivities for ⁵²Cr and the ratio ⁵⁹Co/⁵²Cr were measured at various CRI gas flow rates (through the tip of both skimmer and sampler cones). The testing solution contained 10 µg/L Co in a matrix solution of 1% v/v HNO₃, 1% v/v HCl and 1% v/v IPA. Helium is used as the CRI gas. Since no chromium is present in the test solution, the response for ⁵²Cr⁺ is mostly due to polyatomic interference ions, such as ⁴⁰Ar¹²C⁺, ³⁸Ar¹⁴N⁺ and ³⁵Cl¹⁶O¹H⁺.

As clearly seen in Figure 1 (A), the apparent signal for ⁵²Cr⁺ (actually from interference ions) is decreasing with increasing He flow at the tip of the skimmer cone. When the He flow rate is over 120 mL/min, the interference at ⁵²Cr⁺ is reduced to negligible levels. He flow at the sampler cone tip has little impact on the ⁵²Cr⁺ signal. The efficiency of interference reduction is also demonstrated in Figure 1 (B), where the signal ratio of ⁵⁹Co/⁵²Cr⁺ (i.e., ratio of the signal from a real analyte to the signal from the interfering ions) is improving with increasing He flow rate at the skimmer. Again the He flow at the sampler has no

significant effect on the signal ratio. Therefore, only injecting He gas at the tip of the skimmer cone is used in this work. From Figure 1 (B), when the He flow rate is around 130 mL/min injected at the skimmer cone, the signal ratio of ⁵⁹Co/⁵²Cr⁺ reaches a maximum value, hence a flow rate of 130 mL/min was selected for the following urine sample analysis.

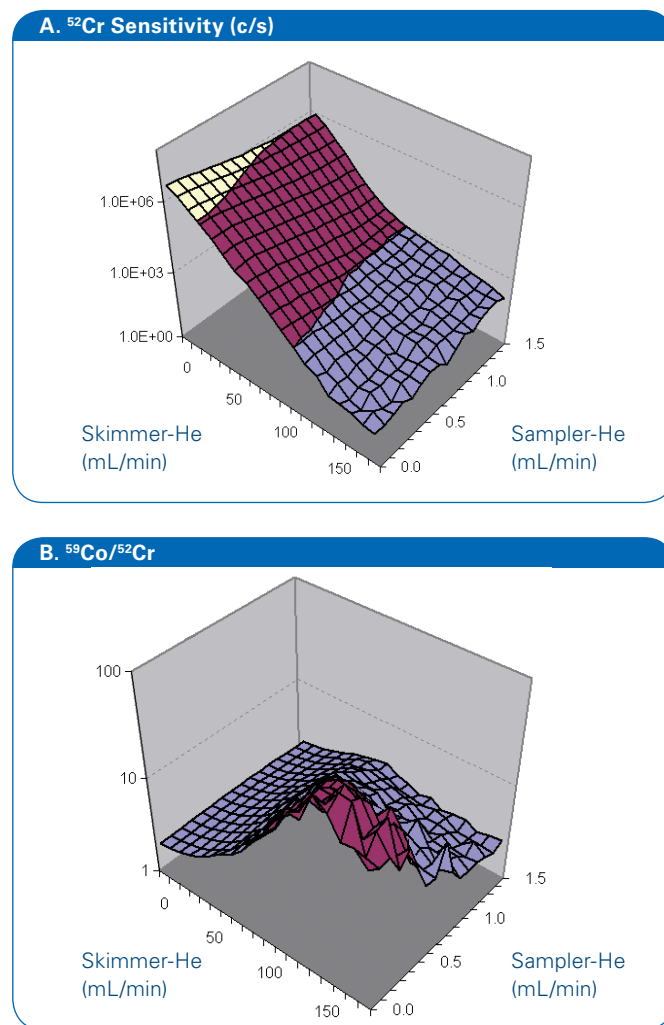


Figure 1. Typical three-dimensional graphs of isotope sensitivity (A) and ratio (B) versus CRI gas-He flow at skimmer and sampler cones.

Sample analysis

Urine metal control materials, UMC L-1 and UMC L-2, were reconstituted according to the supplied procedure. For trace metals determination with the Bruker 820-MS, the urine solution was further diluted by a factor of 1:10, by adding 1 mL of the urine into a pre-cleaned tube containing 9 mL of 2% v/v HNO₃.

This diluted urine solution was used as the sample for direct ICP-MS analysis. As mentioned earlier, the calibration solutions were prepared simply in 2% v/v HNO₃. The metal concentrations measured in the urine metal control materials using the Bruker 820-MS are listed in Table 2. The measured values shown in Table 2 are the average of two repeat measurements.

As seen from Table 2, excellent agreement between the measured and the certified values is observed. The concentration values measured in the two UMC materials are within the certified ranges, except for nickel in UMC L-1 and selenium in UMC L-2. The measured concentrations for Ni in UMC L-1 and Se in UMC L-2 are slightly lower than the certified range. This difference is possibly due to the different techniques used to certify the reference materials as the values for both Ni and Se were certified using atomic absorption spectroscopy rather than ICP-MS.

Element	Measured (µg/L)	Certified (µg/L)	Measured (µg/L)	Certified (µg/L)
²⁴ Mg	51900	46300–69400	206000	185000–277000
²⁷ Al	27.0	23–34	53.0	37–60
⁵² Cr	1.11	0.9–1.3	18.9	16.8–25.3
⁵⁵ Mn	6.27	5.9–8.9	17.1	12.7–19.0
⁵⁹ Co	6.53	6.0–9.0	18.4	16.7–25.0
⁶⁰ Ni	1.44	1.7–2.5	20.6	19.3–29.0
⁶⁵ Cu	7.18	7.0–10	48.1	41–61
⁶⁶ Zn	437	356–535	886	700–1050
⁷⁵ As	65.6	51–77	161	122–183
⁷⁸ Se	51.6	38–57	171	187–281
¹¹¹ Cd	8.58	7.3–11.0	17.3	13.9–20.9
¹²¹ Sb	9.82	6.9–10.4	38.1	26.7–40.0
²⁰⁵ Tl	8.35	6.8–10.1	166	128–193
²⁰⁶⁺⁷⁺⁸ Pb	12.2	10.4–15.6	62.1	51.4–77.1

Table 2. Metal element concentrations measured in Lyphochek® Urine Metals Control, Level-1 and Level-2

Conclusion

This work has successfully demonstrated that the Bruker 820-MS with CRI technology provides a simple and very effective solution for the direct determination of trace elements in complex samples such as urine. Bruker's CRI does not use a pressurized multipole before the mass analyzer. Instead, reaction/collision gases are injected directly into the plasma through the tips of the interface cones. This simple and innovative approach reduces interferences before the ions are extracted into the ion optics.

Additionally, Bruker's CRI technology provides many operational advantages, such as low maintenance, easy operation and eliminates use of corrosive or expensive gases such as ammonia or methane. CRI requires no additional cleaning as it forms part of routine maintenance of the interface cones. Vacuum shutdown is not required, as there is no need to access the vacuum chamber. This reduces potential contamination of the mass analyzer and ion optics within the vacuum chamber. The Bruker 820-MS system can be up and running immediately after cleaning the CRI cones.

References

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Keywords

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Instrumentation & Software

Bruker 820-MS
ICP-MS Expert software

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