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Evaluation of the multi-element capabilities of collision/reaction cell inductively coupled plasma - mass spectrometry in wine analysis

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Abstract

This work explores the multi-element capabilities of inductively coupled plasma - mass spectrometry with collision/reaction cell technology (CCT-ICP-MS) for the simultaneous determination of both spectrally interfered and non-interfered nuclides in wine samples using a single set of experimental conditions. The influence of the cell gas type (i.e. He, He + H₂ and He + NH₃), cell gas flow rate and sample pre-treatment (i.e. water dilution or acid digestion) on the background-equivalent concentration (BEC) of several nuclides covering the mass range from 7 to 238 u has been studied. Results obtained in this work show that, operating the collision/reaction cell with a compromise cell gas flow rate (i.e. 4 mL min⁻¹) improves BEC values for interfered nuclides without a significant effect on the BECs for non-interfered nuclides, with the exception of the light elements Li and Be. Among the different cell gas mixtures tested, the use of He or He + H₂ is preferred over He + NH₃ because NH₃ generates new spectral interferences.

No significant influence of the sample pre-treatment methodology (i.e. dilution or digestion) on the multi-element capabilities of CCT-ICP-MS in the context of simultaneous analysis of interfered and non-interfered nuclides was observed. Nonetheless, sample dilution should be kept at minimum to ensure that light nuclides (e.g. Li and Be) could be quantified in wine. Finally, a direct 5-fold aqueous dilution is recommended for the simultaneous trace and ultra-trace determination of spectrally interfered and non-interfered elements in wine by means of CCT-ICP-MS. The use of the CCT is mandatory for interference-free ultra-trace determination of Ti and Cr. Only Be could not be determined when using the CCT due to a deteriorated limit of detection when compared to conventional ICP-MS.

Keywords:

Spectral interference; Collision/reaction cell; ICP-MS; Multi-element analysis; Wine

1. Introduction

The determination of trace and ultra-trace elements in wine is of great importance. On one hand, it allows detection of toxic elements and forms part of product quality control. On the other hand, elemental analysis of wine is also deployed in the context of provenance determination and the related detection of fraud or adulteration [1].

Several techniques have already been employed for characterizing the elemental composition of wine [2,3]. Nowadays, especially inductively coupled plasma – mass spectrometry (ICP-MS) is widely used owing to its low limits of detection (LoDs of ng L⁻¹ level), wide linear dynamic range, multi-element capabilities and its capability of providing isotopic information [4]. However, the analysis of wine by ICP-MS is not straightforward due to the effects caused by the wine matrix [5]. Several strategies have already been employed to address spectral and non-spectral interferences caused by the wine matrix: appropriate sample pre-treatment [6], targeted optimization of the

operating conditions, e.g. use of cool plasma conditions, optimizing the nebulizer gas flow rate) [7,8], the use of aerosol desolvation [8,9] or electrothermal vaporization [10], the use of mathematical equations for interference correction [11] or the use of an ICP-MS instrument equipped with a sector field mass spectrometer operating at higher mass resolution [12,13].

An alternative approach to deal with spectral interferences is the use of collision/reaction cell technology (CCT). This technology has been reviewed in depth by Tanner *et al.*, [14] and is based on the use of a gas-filled multipole (i.e. quadrupole, hexapole or octopole) assembly located in front of the mass analyzer to remove spectral interferences. This strategy includes electron transfer to neutralize interfering ion species, selective gas phase ion/molecule reactions to convert either the analyte or the interfering ion into a reaction product ion characterized by a different mass and the combination of collision with non-reactive gas particles to slow polyatomic ions sufficiently down to realize their subsequent removal via kinetic energy discrimination. Although this technology has been available for more than 10 years, the use of CCT for elemental analysis of wine has been scarce until recently [15-17]. The common strategy is based on the use of different sets of conditions for determining spectrally interfered and non-interfered elements, respectively. The spectrally interfered elements in wine are usually determined with the aid of CCT, whereas non-interfered elements are measured conventionally (i.e. with a vented collision/reaction cell) in a separate run, thus assuring the best LODs for all analytes. Vinković Vrček *et al.*, [15] employed three different sets of conditions for the determination of 24 elements in wine. The CCT was pressurized with He to determine V, Cr, Mn, Fe, Co, Ga and As, whereas H₂ was used as a cell gas for K, Ca and Se determination. Remaining elements (i.e. Na, Mg, Al, Ca, Ni, Cu, Zn, Sr, Mo, Cd, In, Sn, Ba, Tl and Pb) were measured using the conventional mode. A

similar approach was employed by Di Paola-Naranjo *et al.*, [16] but they used a single gas mixture (i.e. He + H₂) to access all interfered nuclides. Although these approaches are completely valid, they are more time-consuming since the multi-element capabilities of ICP-MS are not fully exploited.

Several authors have demonstrated that CCT operating conditions could be successfully optimized to obtain sufficient detection capability for both spectrally interfered and non-interfered isotopes at the same time for aqueous and acid-digested samples [18-21]. Recently, this approach has also been explored for multi-element wine analysis [17]. Several interfered (⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁶Fe, ⁵⁷Fe, ⁵⁸Ni, ⁵⁹Co, ⁶⁰Ni, ⁶⁶Zn) and non-interfered (¹¹¹Cd, ¹¹⁷Sn, ¹¹⁸Sn, ¹¹⁹Sn, ¹²⁰Sn, ¹³³Cs, ²⁰⁵Tl, ²⁰⁸Pb) nuclides have been measured with CCT using a He cell gas flow rate of 4.3 mL min⁻¹. Nonetheless, a higher He gas flow rate (10 mL min⁻¹) was needed to determine the interfered nuclides ⁷⁵As and ⁷⁸Se. No detailed information was provided on how detection capability for various nuclides was affected by the CCT operating conditions and, hence, the need of using different sets of conditions to determine the selected analytes in wine was not demonstrated. Finally, it is also worth to mention that contradictory conclusions as to the optimum ICP-MS conditions for the determination of some elements can be found in the literature. For instance, determination of Mn, Ni, Zn, Sr, Mo, Cd, Ba and Pb has been carried out using either conventional ICP-MS [15] or CCT-ICP-MS [16,17].

The goal of this work was to evaluate the multi-element capabilities of CCT-ICP-MS for simultaneous determination of both spectrally interfered and non-interfered nuclides in wine samples using a single set of experimental conditions. To this end, the influence of the type of cell gas (i.e. He, He + H₂, He + NH₃) and the flow rate on the background-equivalent concentration (BEC) was studied for several interfered and non-interfered nuclides, covering the mass range from 7 to 238 u, both after aqueous dilution

of the wine sample and after acid digestion. Subsequently, the methodology selected was applied to the determination of 56 elements (Li, Be, B, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Pd, Ag, Cd, In, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Os, Ir, Pt, Tl, Pb, Bi, Th and U) in different wine samples.

2. Experimental

2.1 Reagents

High purity water (≥ 18.2 M Ω .cm resistivity) obtained from a Direct-Q3 Milli-Q Element water purification system (Millipore S.A., Paris, France), ethanol (anhydrous, Sigma-Aldrich, Steinheim, Germany) and sub-boiled 70% w w⁻¹ nitric acid (Chem-Lab, Germany) were employed throughout the work to prepare synthetic “wine matrix” solutions. In addition, to simulate the composition of wine, also sodium chloride, magnesium chloride hexahydrate, potassium nitrate and calcium nitrate tetrahydrate (Suprapur, Merck, Darmstadt, Germany) were employed. Li, Be, B, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Tl, Pb, Bi, Th and U 1 g L⁻¹ mono-element stock solutions (J.T. Baker, Deventer, Netherlands) were used to prepare a multi-element standard solution. He, He + H₂ (7.0% v v⁻¹) and He + NH₃ (0.9% v v⁻¹) gas mixtures (Air Liquide, Belgium) were used as collision/reaction cell gases.

2.2 ICP-MS instrumentation

A quadrupole-based Xseries2 ICP-MS instrument (Thermo Scientific, Germany) equipped with Ni cones and a hexapole collision/reaction cell was employed throughout this work. This instrument was operated both with a vented and with a pressurized cell.

In the following paragraphs, the use of a vented cell and a pressurized cell will be noted as non-CCT and CCT, respectively. Table 1 shows the operating conditions employed. Experimental conditions for both CCT and non-CCT mode were optimized daily according to the protocol described in the user's manual. Thus, when the collision/reaction cell was operated with He or He + H₂, the cell gas flow rate was adjusted to 4 mL min⁻¹ and the lens settings were modified to minimize the background signal at $m/z = 78$ (i.e. ⁷⁸Ar₂⁺). The optimization procedure for He + NH₃ was slightly different. The cell gas flow rate was set at 8 mL min⁻¹ and the lens settings were modified to minimize the background at $m/z 51$ (i.e. ³⁵Cl¹⁶O⁺) while aspirating a 1% v v⁻¹ HCl solution.

2.3. Synthetic wine matrix solutions

The study of the multi-element capabilities of CCT-ICP-MS for elemental analysis of wine was carried out using three different synthetic wine matrix solutions: (i) 2.5% v v⁻¹ ethanol plus 400 mg L⁻¹ of K, 20 mg L⁻¹ of Ca and of Mg and 4 mg L⁻¹ of Na; (ii) 1.2% v v⁻¹ ethanol plus 200 mg L⁻¹ of K, 10 mg L⁻¹ of Ca and of Mg, and 2 mg L⁻¹ of Na. These solutions represent the matrices obtained after 5-fold and 10-fold wine dilution with high purity water, respectively (i.e. the most widely employed dilution factors reported in the literature to reduce non-spectral interferences when dealing with elemental analysis of wine [6,8,22]); and (iii) a 7% w w⁻¹ nitric acid solution plus 200 mg L⁻¹ of K, 10 mg L⁻¹ of Ca and of Mg, and 2 mg L⁻¹ of Na. This represents the matrix obtained after nitric acid digestion of 5 mL of wine followed by aqueous dilution to 50 mL (thus corresponding to 10-fold sample dilution) [8]. The solutions contained 100 µg L⁻¹ of each of the elements composing the multi-element standard solution described in section 2.1.

2.4. Wine samples

Three different wine samples were analyzed: a white one (Bergerac, 2012, France) and two red ones (Montepulciano d'Abruzzo, 2012, Italy and Ramiro II, 2006, Spain). These samples were chosen for a proof-of-concept study as they cover a range of matrix characteristics and origins. Samples were acquired at a local supermarket. The ethanol content of the wines ranged between 11 and 13% v v⁻¹. The wine samples were analyzed after 5-fold dilution with Mili-Q water.

2.5. Calibration

The analysis of wine samples was based on external calibration using matrix-matched standard solutions and internal standardization to correct for matrix effects and signal drift. Scandium, Rh, Te and Re were tested as internal standards. The concentration of each internal standard was 100 µg L⁻¹.

3. Results and discussion

3.1. CCT optimization for wine analysis

Figure 1 shows the influence of the cell gas (He + H₂ mixture) flow rate on the background equivalent concentration (BEC) for some selected interfered nuclides (⁵²Cr⁺, ⁵⁵Mn⁺, ⁵⁶Fe⁺, ⁶⁰Ni⁺, ⁶³Cu⁺ and ⁷⁸Se⁺) measured in the synthetic 10-fold diluted wine matrix containing 1.2% v v⁻¹ ethanol. BEC values were calculated using the net analyte signals and the corresponding blank signals as [21]:

$$BEC(\mu\text{g L}^{-1}) = \frac{\text{Analyte concentration} \cdot \text{Background signal}}{\text{Net analyte signal}}$$

Signals for these nuclides are interfered by polyatomic ions ($^{40}\text{Ar}^{12}\text{C}^+$, $^{39}\text{K}^{16}\text{O}^+$, $^{40}\text{Ar}^{16}\text{O}^+ / ^{40}\text{Ca}^{16}\text{O}^+$, $^{44}\text{Ca}^{16}\text{O}^+ / ^{23}\text{Na}^{37}\text{Cl}^+$, $^{40}\text{Ar}^{23}\text{Na}^+$ and $^{40}\text{Ar}^{38}\text{Ar}^+$), originating from the plasma gas (Ar), entrained air (N_2 and O_2) and/or the wine matrix (H_2O , inorganic salts and organic compounds) [23]. As shown in Figure 1, the BEC values for $^{55}\text{Mn}^+$, $^{56}\text{Fe}^+$, $^{60}\text{Ni}^+$ and $^{63}\text{Cu}^+$ decrease with increasing cell gas flow rate up to 4 mL min^{-1} and then remain more or less constant. On the other hand, the BECs for $^{52}\text{Cr}^+$ and $^{78}\text{Se}^+$ decrease up to the maximum gas flow rate of 8 mL min^{-1} used in our experiments. The effect of the cell gas flow on the corresponding background and net analyte signals is presented in Figure S1a and S1b, respectively (see Appendix). Irrespective of the m/z considered, the background intensity is reduced when increasing the cell gas flow rate. This is caused by: (i) ion scattering, (ii) reaction with the cell gas (e.g. Ar^+ with H_2) and/or (iii) the use of a decelerating potential barrier [14]. Analyte ions are also affected by scattering, but they are less influenced than polyatomic ions due to their smaller size. In addition, at relatively low cell pressure, the cell gas has a beneficial effect on the analyte ion transmission efficiency as a result of collisional focusing [14].

From the results shown in Figure 1, it is clear that the selection of one cell gas flow rate with minimum BECs for all interfered nuclides is not possible and thus, compromise conditions need to be used. A detailed inspection of the results obtained at 4 and 8 mL min^{-1} reveals that the use of 8 mL min^{-1} cell gas flow rate must be discarded due to its negative impact on the sensitivity for most of the nuclides studied. Thus, for instance, when increasing the cell gas flow rate from 4 to 8 mL min^{-1} , ion signal intensities decrease 20- to 4-fold for $^7\text{Li}^+$ and $^{208}\text{Pb}^+$, respectively. Such behaviour has also been observed when operating with the other cell gases tested (i.e. He and He + NH_3).

Figure 2 shows the BEC_{rel} values, defined as the ratio between the BECs measured in CCT-mode to those in non-CCT mode, for both interfered and non-interfered nuclides

(⁷Li, ⁹Be, ¹¹B, ²⁷Al, ⁴⁵Sc, ⁴⁷Ti, ⁵¹V, ⁵²Cr, ⁵³Cr, ⁵⁵Mn, ⁵⁶Fe, ⁵⁷Fe, ⁵⁹Co, ⁶⁰Ni, ⁶²Ni, ⁶³Cu, ⁶⁵Cu, ⁶⁶Zn, ⁶⁷Zn, ⁶⁸Zn, ⁶⁹Ga, ⁷¹Ga, ⁷²Ge, ⁷³Ge, ⁷⁵As, ⁷⁷Se, ⁷⁸Se, ⁸⁰Se, ⁸²Se, ⁸⁵Rb, ⁸⁶Sr, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹¹Zr, ⁹³Nb, ⁹⁵Mo, ⁹⁷Mo, ¹⁰¹Ru, ¹⁰³Rh, ¹⁰⁵Pd, ¹⁰⁷Ag, ¹¹¹Cd, ¹¹⁵In, ¹¹⁸Sn, ¹²⁰Sn, ¹²¹Sb, ¹²⁸Te, ¹³³Cs, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴³Nd, ¹⁴⁶Nd, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁷Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ¹⁸¹Ta, ¹⁸²W, ¹⁸⁵Re, ¹⁸⁹Os, ¹⁹³Ir, ¹⁹⁵Pt, ²⁰⁵Tl, ²⁰⁸Pb, ²⁰⁹Bi, ²³²Th and ²³⁸U) when operating with different cell gases (i.e. He + H₂, He and He + NH₃) at 4 mL min⁻¹. BEC repeatability was ≈20% RSD. Therefore, it can be considered that BEC_{rel} values lower than 0.6 (i.e. exceeding an uncertainty range of ±40%) indicate that the CCT mode decreases (i.e. improves) the BEC when compared to the non-CCT mode. On the other hand, BEC_{rel} values higher than 1.4 indicate that the CCT mode deteriorates the BEC when compared to the non-CCT mode. This range is represented by dashed lines in Fig. 2. In general, and irrespective of the cell gas used, nuclides below 95 u are affected by the use of CCT (i.e. BEC_{rel} ≠ 1.0). For nuclides above m/z 95, there is no significant difference between the BEC values observed in CCT and non-CCT mode (i.e. BEC_{rel} = 1.0). Among the nuclides with m/z < 95, using CCT has a beneficial effect on the BEC values for several nuclides (⁵²Cr, ⁵³Cr, ⁵⁵Mn, ⁵⁶Fe, ⁵⁷Fe, ⁶⁰Ni, ⁶⁷Zn, ⁶⁹Ga, ⁷³Ge, ⁷⁵As, ⁷⁷Se, ⁷⁸Se, ⁹⁰Zr⁺ and ⁹⁵Mo⁺) when compared to non-CCT conditions. However, the BEC values obtained with CCT for ⁷Li⁺, ⁹Be⁺, ⁴⁵Sc⁺ and ⁸²Se⁺ were deteriorated (BEC_{rel} > 1.4). These results can be explained taking into account how background and analyte signals are affected by the cell gas flow. For ⁷Li⁺, ⁹Be⁺ and ⁴⁵Sc⁺, the analyte ion scattering is more significant than background reduction, hence, the BECs with CCT were higher than those without CCT [14]. For other nuclides (¹¹B⁺, ²⁷Al⁺, ⁴⁷Ti⁺, etc.), the effect of using CCT on background and analyte signal was similar and thus, no significant change in the BEC was observed.

The results depicted in Figure 2 reveal that the use of He + NH₃ mixture as cell gas provides more nuclides with $BEC_{rel} > 1.4$ (⁷Li⁺, ⁹Be⁺, ⁵⁵Mn⁺, ⁵⁷Fe⁺, ⁵⁹Co⁺, ⁶⁰Ni⁺, ⁶⁸Zn⁺, ⁷²Ge⁺, ⁷³Ge⁺, ⁸⁹Y⁺, ⁹⁰Zr⁺ and ⁹¹Zr⁺) than using He + H₂ or He. This is due to new interferences caused by NH₃ (i.e. higher background is observed) [14,19]. The BEC values obtained with He + H₂ and He were similar and, hence, both gas mixtures are suitable for multi-element analysis of wine.

3.2. Influence of the matrix composition

Different protocols for digestion or dilution aiming to mitigate non-spectral interferences are reported as sample pre-treatment in the literature [3]. In this work, in addition to the synthetic 10-fold diluted wine matrix containing 1.2% v v⁻¹ ethanol, alternative matrix solutions have been employed to check the influence of the sample preparation methodology on CCT multi-element capabilities. To this end, a synthetic 5-fold diluted wine solution in 2.5% v v⁻¹ ethanol and a synthetic digested wine solution in 7% w w⁻¹ nitric acid (see Section 2.3) were tested. Figure 3 shows BEC_{rel} values for all nuclides obtained with these matrices and using the He + H₂ cell gas mixture (4 mL min⁻¹). The results were, generally speaking, similar to those found for the synthetic 10-fold diluted wine solution containing 1.2% v v⁻¹ ethanol (Figure 2).

3.3 Limits of detection (LoDs)

From the results shown in Figure 1 and Figure 2, it is clear that BEC values obtained with CCT do not significantly depend on the matrix composition (i.e. dilution or digestion). Nonetheless, to select the most suitable sample preparation methodology for wine analysis with CCT, the LoDs for each element have been calculated and compared with the typical element concentration in this type of samples. Table 2 shows the LoDs

for the different nuclides in each of the matrices tested. These LoDs were calculated using the calibration graph according to the method described by Hubaux and Vos (i.e. based on 5 standards, 95% confidence level) [24]. In general, the LoDs for the synthetic 5-fold diluted wine matrix containing 2.5% v v⁻¹ ethanol are slightly lower than those obtained for the synthetic 10-fold diluted wine matrix. This is in agreement with the analyte dilution factor employed. The LoDs obtained for the synthetic digested wine solution in 7% w w⁻¹ nitric acid are similar to the values obtained with the 10-fold diluted wine matrix containing 1.2% v v⁻¹ ethanol. LoDs for ⁵²Cr⁺ and ⁵³Cr⁺ were higher when operating with the 2.5% v v⁻¹ ethanol matrix due to the higher background signals observed (i.e. ⁴⁰Ar¹²C⁺ and ⁴⁰Ar¹³C⁺, respectively). No significant differences were observed between CCT (Table 2) and non-CCT (Table S1, Appendix) conditions for non-interfered nuclides, with the exception of the light elements Li and Be. The LoDs for these elements were 100-fold higher under CCT than under non-CCT conditions. Differences between CCT and non-CCT LoDs for Li and Be were already reported earlier for deionized water and diluted acid solutions, but they were less substantial (factor of 3-10) [18,19].

LoDs for simultaneous multi-element analysis of wine by CCT-ICP-MS have not been previously reported in the literature. Nonetheless, the LoDs for non-interfered nuclides in the synthetic 10-fold diluted wine matrix solution are of the same order of magnitude as those previously published for some of the elements using conventional ICP-MS (i.e. non-CCT) [11,25-27]. The LoDs listed in Table 2 are below the concentration levels usually found for these elements in wines, with the exception of Li and Be [3,28]. The Li concentration levels in wine are usually above 10 µg L⁻¹, whereas Be concentrations do not exceed 5 µg L⁻¹. Among the different sample matrices studied the synthetic 5-fold diluted wine matrix provides the lowest LoDs for Li (6-7 µg L⁻¹) and, therefore,

this element can be measured simultaneously with the other elements using a single set of experimental conditions. Unfortunately, this approach is not successful for Be (LoD: $20 \mu\text{g L}^{-1}$). The use of lower dilution factors (i.e. higher ethanol content or higher acid concentrations) to further improve the LoDs for these elements was not explored to avoid enhancement of non-spectral interferences (i.e. signal suppression) and maintain long-term instrument performance. From these results, and taking into account sample preparation simplicity, 5-fold aqueous dilution of wine (i.e. 2.5% v v⁻¹ ethanol remaining) seems the best sample pre-treatment approach for wine analysis with CCT-ICP-MS.

3.4. Analysis of the wine samples

Different wine samples were analyzed using the selected compromise CCT conditions (He + H₂, 4 mL min⁻¹) after 5-fold dilution with Mili-Q water (i.e. 2.5% ethanol content). External calibration was based on the use of the corresponding synthetic wine matrix-matched standards. Four internal standards (Sc, Rh, Te and Re) (IS) were employed to cover the m/z range. For each nuclide, IS selection was based on m/z closeness [29]. Relative standard deviations (RSD) were checked for 2.5% v v⁻¹ ethanol solutions containing different analyte concentrations (see Table S2, Appendix). In general, for analyte concentrations above $1 \mu\text{g L}^{-1}$, RSD values were less than 3%. For analytes with a concentrations below $0.05 \mu\text{g L}^{-1}$ the precision was deteriorated (5-7%). A recovery test was performed to evaluate method accuracy because no certified wine material is available for validating the multi-element analysis of wine samples. To this end, and taking into account the concentrations usually found in wine for each analyte, 5-fold diluted samples were spiked at different concentration levels (0.1, 10, 100 and $500 \mu\text{g L}^{-1}$) with a multi-element standard solution (see par 2.1.). Recoveries for all the

elements in the three wine samples studied in this work were almost quantitative, ranging from $107\pm 3\%$ ($^{47}\text{Cr}^+$) to $92\pm 4\%$ ($^{209}\text{Bi}^+$) (see Table S2, Appendix).

Table 3 shows the results of the elemental analysis of different wine samples with CCT-ICP-MS. In general terms, the concentration levels for trace and ultra-trace levels found in these wine samples are similar to those reported previously in the literature [8,22,30]. Beryllium, Ag, Os and Ir were not detected in the wine samples whereas Li, Ru, Pd, In, Pt, Bi and Tl were only detected in some wines. Isotope selection did not have any influence on the analytical results, with the exception of Ga and Se. Gallium concentrations based on $^{69}\text{Ga}^+$ monitoring were between 47 and 100-fold times higher than those obtained using the $^{71}\text{Ga}^+$ isotope, suggesting the occurrence of some kind of a non-mitigated spectral interference with the CCT at m/z 69. This interference may be related to $^{138}\text{Ba}^{2+}$ due to the relatively high levels of Ba (i.e. $\approx 100 \mu\text{g L}^{-1}$) in wine compared to Ga [11]. To check this hypothesis, the $^{69}\text{Ga}^+$ signal was monitored for a synthetic wine solution containing only $20 \mu\text{g L}^{-1}$ of Ga as well as for a solution containing $20 \mu\text{g L}^{-1}$ of Ga spiked with 100mg L^{-1} of Ba. The results showed that the $^{69}\text{Ga}^+$ signal for the Ga $20 \mu\text{g L}^{-1}$ standard solution spiked with Ba was enhanced 2-fold when compared to the un-spiked solution. Therefore, it could be concluded that, for elemental wine analysis, the ^{71}Ga isotope should be preferred over $^{69}\text{Ga}^+$. Though isotopic abundance of $^{69}\text{Ga}^+$ is higher than that of $^{71}\text{Ga}^+$, LoDs for the latter isotope with CCT-ICP-MS are low enough to quantify Ga at the levels usually found in wine (i.e. $0.4\text{-}7 \mu\text{g L}^{-1}$ range) [11,22]. Selenium determination was feasible using most of the isotopes studied ($^{77}\text{Se}^+$, $^{78}\text{Se}^+$ and $^{82}\text{Se}^+$). For $^{80}\text{Se}^+$ the concentrations found in the wine samples were below the LoD.

For comparison purposes, the wine samples were also analyzed without the assistance of the CCT, see Table S3, Appendix). In general, the results obtained with and without

CCT were not statistically different (95% confidence level, 3 replicates). Nonetheless, some differences were noticed. The LoDs attainable with conventional ICP-MS are low enough to allow Li and Be determination in the wine samples. The Ti and Cr concentration values obtained via $^{47}\text{Ti}^+$ and $^{53}\text{Cr}^+$ with non-CCT ICP-MS seem to be affected by the occurrence of spectral interference since they are systematically higher than those observed with CCT. It is well-known that Cr isotopes are interfered by carbon-based ($^{40}\text{Ar}^{12}\text{C}^+$ and $^{40}\text{Ar}^{13}\text{C}^+$) interferences [8]. In fact, $^{52}\text{Cr}^+$ determination with non-CCT was not feasible due to the high background (i.e. high LoD). The origin of the spectral interference on $^{47}\text{Ti}^+$ was investigated and seems to be caused by $^{31}\text{P}^{16}\text{O}^+$, since the P levels in wine are usually high (50-200 mg L⁻¹) [27,28]. In fact, it was observed that the $^{47}\text{Ti}^+$ signal intensity for a 20 µg L⁻¹ of Ti solution spiked with P (100 mg L⁻¹) was enhanced 2.5 fold when compared to the corresponding unspiked solution. Though Fe, Cu and Zn isotopes are expected to be subject to spectral interference ($^{40}\text{Ar}^{16}\text{O}^+$, $^{40}\text{Ar}^{23}\text{Na}^+$, $^{40}\text{Ca}^{16}\text{O}^+$, etc.), the concentration values for these elements (ppm range) are relative high in comparison with LoDs and, therefore, no significant difference was observed between the CCT and non-CCT results. Finally, it is worth mentioning that Se determination with non-CCT ICP-MS was only feasible using $^{77}\text{Se}^+$ and $^{82}\text{Se}^+$. The LoDs for the other Se isotopes do not allow analyte quantification.

4. Conclusions

Results of this work illustrate that multi-element capabilities of ICP-MS can be fully exploited for the simultaneous trace and ultra-trace determination of 55 elements in wine samples (Li, B, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Pd, Ag, Cd, In, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Os, Ir, Pt, Tl, Pb, Bi, Th and U) using a He+H₂-pressurized

collision/reaction cell. The simultaneous analysis of interfered and non-interfered elements with CCT can be accomplished using a compromise cell gas flow rate and low-reactive gas mixtures (e.g. He or He+H₂). Via appropriate selection of the experimental conditions, no significant differences in LoDs for non-interfered elements were established between conventional ICP-MS and CCT-ICP-MS.

A direct 5-fold wine dilution is recommended for the simultaneous trace and ultra-trace determination of spectrally interfered and non-interfered elements in wine by means CCT-ICP-MS. CCT is mandatory for determination of spectrally-interfered elements, such as Cr and Ti, at ultra-trace levels in wine. Only Be determination was not feasible under compromise CCT conditions because the levels usually found in wine for this element were below the LoD.

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Figure captions

Figure 1. Influence of the cell gas flow rate on the background-equivalent concentration (BEC) for several interfered nuclides measured in CCT mode using a 1.2 v v⁻¹ ethanol plus 200 mg L⁻¹ of K, 10 mg L⁻¹ of Ca and of Mg, and 2 mg L⁻¹ of Na matrix solution. Gas type: He + H₂ (7% v v⁻¹).

Figure 2. Ratio of background-equivalent concentrations (BEC_{rel}), i.e. BEC obtained in CCT mode / BEC in non-CCT mode, as a function of the m/z ratio for a 1.2 v v⁻¹ ethanol plus 200 mg L⁻¹ of K, 10 mg L⁻¹ of Ca and of Mg, and 2 mg L⁻¹ of Na matrix solution using different cell gases (●) He + H₂; (◆) He; (■) He + NH₃. Cell gas flow rate: 4 mL min⁻¹.

Figure 3. Ratio of background-equivalent concentrations (BEC_{rel}), i.e. BEC obtained in CCT mode / BEC in non-CCT mode, as a function of m/z for (■) a 2.5% v v⁻¹ ethanol plus 400 mg L⁻¹ of K, 20 mg L⁻¹ of Ca and of Mg and 4 mg L⁻¹ of Na matrix (◆) a 7% w w⁻¹ nitric acid solution plus 200 mg L⁻¹ of K, 10 mg L⁻¹ of Ca and of Mg, and 2 mg L⁻¹ of Na matrix. Gas type: He + H₂ (7% v v⁻¹); cell gas flow rate: 4 mL min⁻¹.

Table 1. ICP-MS operating conditions

Thermo XSeries 2 ICP-MS		
	Non-CCT	CCT
Plasma forward power (W)	1400	
Argon flow rate (L min⁻¹)		
Plasma	13.00	
Auxiliary	0.70	
Nebulizer	0.82 ^{&} -0.87 ^{\$}	
Sample uptake rate (mL min⁻¹)	0.500	
Lens potential (V)		
Extraction	-110	
Lens 1	-1230	
Focus	10.4	-7.8 [#] /-15 [*]
D1	-43.1	-43.1 [#] /-43.9 [*]
Pole Bias	-3.9	-17 [#] /-20 [*]
Hexapole Bias	-1.4	-20 [#] /-19 [*]
Lens 2	-80.8	-80.8 [#] /-76.9 [*]
Lens 3	-195.3	
D2	-133	-107 [#] /-102 [*]
DA	-43.1	
CCT gas type	N/A	He He + H ₂ (7.0%) He + NH ₃ (0.9%)
CCT gas flow rate (mL min⁻¹)	N/A	0-8
Dwell time (ms)	15	
Sweeps	100	
Replicate measurements	3	

& nitric acid (digested wine); \$ ethanol solutions (diluted wine)

He and He + H₂; * He + NH₃

Table 2. Limits of detection for synthetic diluted and acid-digested wine matrices obtained via CCT-ICP-MS. Cell gas: He + H₂; cell gas flow rate: 4 mL min⁻¹.

Element	m/z	Limit of detection ($\mu\text{g L}^{-1}$)		
		Ethanol		Nitric acid
		2.5% v v ⁻¹	1.2% v v ⁻¹	7% w w ⁻¹
Li	7	6	20	40
Be	9	20	30	30
B	11	0.5	0.8	1
Al	27	8	7	6
Ti	47	0.1	0.3	1
V	51	0.05	0.2	0.5
Cr	52	7	1	0.7
Cr	53	0.7	0.3	0.4
Mn	55	0.1	0.5	0.4
Fe	56	2	4	4
Fe	57	60	80	50
Co	59	0.03	0.07	0.1
Ni	60	0.3	1	0.9
Ni	62	2	4	3
Cu	63	0.2	0.5	0.6
Cu	65	0.3	0.7	0.6
Zn	66	0.2	0.5	2
Zn	67	1	4	4
Zn	68	0.2	1	1
Ga	69	0.02	0.03	0.05
Ga	71	0.03	0.05	0.05
Ge	72	0.02	0.04	0.1
Ge	73	0.06	0.1	0.2
As	75	0.02	0.06	0.06
Se	77	0.09	0.5	0.6
Se	78	0.05	0.1	0.2
Se	80	0.8	2	3
Se	82	0.06	0.3	0.4
Rb	85	6	7	7
Sr	86	7	10	14
Sr	88	2	3	4
Y	89	0.03	0.05	0.4
Zr	90	0.02	0.06	0.06
Zr	91	0.07	0.1	0.2
Nb	93	0.01	0.03	0.09
Mo	95	0.03	0.08	0.1
Mo	97	0.06	0.2	0.2
Ru	101	0.02	0.04	0.1
Pd	105	0.06	0.09	0.08
Ag	107	0.02	0.05	0.02

Cd	111	0.02	0.04	0.06
In	115	0.03	0.07	0.04
Sn	118	0.2	0.4	0.4
Sn	120	0.2	0.5	0.5
Sb	121	0.04	0.1	0.1
Cs	133	0.03	0.05	0.07
Ba	137	0.1	0.5	0.4
La	139	0.03	0.09	0.04
Ce	140	0.01	0.05	0.06
Pr	141	0.004	0.01	0.005
Nd	143	0.02	0.05	0.03
Nd	146	0.02	0.06	0.03
Eu	153	0.002	0.007	0.005
Gd	157	0.003	0.006	0.006
Tb	159	0.002	0.007	0.006
Dy	163	0.003	0.01	0.02
Ho	165	0.002	0.005	0.006
Er	167	0.005	0.007	0.01
Tm	169	0.004	0.005	0.004
Yb	172	0.004	0.006	0.007
Lu	175	0.002	0.004	0.005
Hf	178	0.006	0.009	0.006
Ta	181	0.01	0.02	0.004
W	182	0.04	0.2	0.07
Os	189	0.09	0.1	0.3
Ir	193	0.01	0.06	0.04
Pt	195	0.02	0.04	0.05
Tl	205	0.003	0.009	0.02
Pb	208	0.06	0.1	0.05
Bi	209	0.03	0.08	0.1
Th	232	0.007	0.01	0.02
U	238	0.009	0.04	0.02

Table 3. Results of the analysis of different wines via CCT-ICP-MS operated under compromise conditions. The precision is presented in the form of $\pm \frac{t \cdot s}{\sqrt{n}}$ confidence intervals, in which t is the Student's t (95% confidence level); s is the standard deviation and n the number of replicates (3). Gas type: He + H₂ (7% v v⁻¹); cell gas flow rate: 4 mL min⁻¹; sample preparation: 5-fold wine dilution.

Element	m/z	Concentration ($\mu\text{g L}^{-1}$)		
		French wine	Italian wine	Spanish wine
Li	7	<LOD	18 \pm 3	30 \pm 3
Be	9	<LOD	<LOD	<LOD
B	11	2200 \pm 200	6800 \pm 300	6900 \pm 200
Al	27	690 \pm 30	520 \pm 30	870 \pm 40
Ti	47	69 \pm 4	61 \pm 4	63 \pm 6
V	51	54.8 \pm 0.08	1.95 \pm 0.10	38.7 \pm 0.6
Cr	52	20.0 \pm 0.6	12.0 \pm 0.2	11.0 \pm 0.4
Cr	53	18.4 \pm 0.6	11.2 \pm 0.3	10.4 \pm 0.8
Mn	55	840 \pm 50	790 \pm 60	1180 \pm 80
Fe	56	1650 \pm 160	2100 \pm 100	4310 \pm 120
Fe	57	1550 \pm 120	2130 \pm 120	4300 \pm 100
Co	59	3.51 \pm 0.14	1.60 \pm 0.04	2.80 \pm 0.08
Ni	60	22.6 \pm 0.6	12.8 \pm 0.6	12.7 \pm 0.3
Ni	62	22.6 \pm 0.8	12.8 \pm 0.6	12.5 \pm 1.2
Cu	63	56 \pm 2	279 \pm 8	289 \pm 6
Cu	65	54 \pm 5	280 \pm 22	288 \pm 12
Zn	66	1410 \pm 50	544 \pm 10	520 \pm 30
Zn	67	1450 \pm 60	540 \pm 30	490 \pm 20
Zn	68	1460 \pm 30	550 \pm 30	500 \pm 20
Ga	69	16.0 \pm 0.6	14.5 \pm 0.4	35.6 \pm 1.2
Ga	71	0.34 \pm 0.03	0.354 \pm 0.016	0.348 \pm 0.018
Ge	72	0.111 \pm 0.005	0.104 \pm 0.008	0.099 \pm 0.005
Ge	73	0.104 \pm 0.006	0.114 \pm 0.006	0.098 \pm 0.004
As	75	5.7 \pm 0.6	1.33 \pm 0.12	2.8 \pm 0.2
Se	77	0.48 \pm 0.02	0.548 \pm 0.009	0.57 \pm 0.02
Se	78	0.48 \pm 0.02	0.543 \pm 0.009	0.57 \pm 0.02
Se	80	<LOD	<LOD	<LOD
Se	82	0.48 \pm 0.01	0.50 \pm 0.03	0.54 \pm 0.03
Rb	85	1000 \pm 90	1780 \pm 80	620 \pm 40
Sr	86	240 \pm 20	590 \pm 40	980 \pm 60
Sr	88	240 \pm 30	560 \pm 50	1000 \pm 40
Y	89	1.13 \pm 0.04	0.301 \pm 0.011	0.807 \pm 0.014
Zr	90	8.40 \pm 0.16	2.21 \pm 0.06	5.11 \pm 0.12
Zr	91	8.4 \pm 0.5	2.27 \pm 0.18	1.96 \pm 0.03
Nb	93	1.80 \pm 0.10	0.200 \pm 0.007	2.7 \pm 0.2
Mo	95	4.7 \pm 0.3	1.77 \pm 0.07	1.98 \pm 0.06

Mo	97	4.6±0.2	1.73±0.4	5.1±0.2
Ru	101	<LOD	0.29±0.03	<LOD
Pd	105	0.43±0.08	<LOD	0.35±0.05
Ag	107	<LOD	<LOD	<LOD
Cd	111	0.20±0.02	0.111±0.004	0.117±0.007
In	115	0.050±0.008	<LOD	<LOD
Sn	118	2.8±0.02	1.85±0.11	2.69±0.15
Sn	120	2.83±0.05	1.84±0.07	2.8±0.2
Sb	121	0.75±0.03	0.281±0.019	0.425±0.012
Cs	133	3.51±0.08	4.37±0.14	3.60±0.03
Ba	137	101±14	92±7	200±20
La	139	1.245±0.018	0.104±0.008	1.242±0.018
Ce	140	2.49±0.18	0.215±0.004	2.488±0.013
Pr	141	0.30±0.03	0.033±0.005	0.269±0.008
Nd	143	1.15±0.02	0.121±0.007	1.009±0.011
Nd	146	1.13±0.02	0.124±0.019	1.01±0.02
Eu	153	0.084±0.006	0.027±0.002	0.096±0.006
Gd	157	0.227±0.006	0.038±0.005	0.185±0.006
Tb	159	0.035±0.005	0.0085±0.0006	0.036±0.006
Dy	163	0.221±0.002	0.0123±0.0019	0.0334±0.0008
Ho	165	0.047±0.001	0.057±0.003	0.170±0.003
Er	167	0.156±0.015	0.036±0.004	0.099±0.003
Tm	169	0.026±0.002	0.007±0.001	0.0140±0.0002
Yb	172	0.157±0.005	0.044±0.001	0.095±0.004
Lu	175	0.026±0.002	0.010±0.002	0.0147±0.002
Hf	178	0.324±0.016	0.092±0.002	0.150±0.010
Ta	181	0.306±0.014	0.158±0.004	0.117±0.008
W	182	3.50±0.02	0.83±0.06	1.89±0.04
Os	189	<LOD	<LOD	<LOD
Ir	193	<LOD	<LOD	<LOD
Pt	195	<LOD	<LOD	0.236±0.004
Tl	205	0.500±0.012	0.408±0.013	<LOD
Pb	208	20.8±0.6	9.5±0.4	7.03±0.2
Bi	209	0.241±0.009	<LOD	<LOD
Th	232	0.134±0.008	0.033±0.004	0.17±0.04
U	238	0.518±0.019	0.333±0.013	0.733±0.014

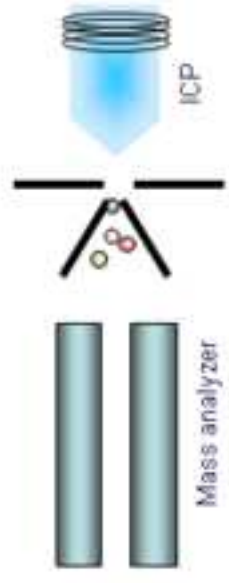
Highlights

- Multi-element capabilities of CCT-ICP-MS successfully checked for wine analysis
- Simultaneous determination of spectrally interfered and non-interfered elements feasible
- CCT-ICP-MS is required for Ti and Cr ultra-trace analysis in wine
- Be determination in wine by means CCT-ICP-MS is not feasible

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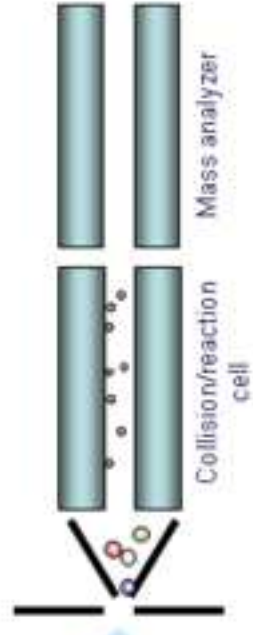
NON-INTERFERED NUCLIDES

Conventional ICP-MS



INTERFERED NUCLIDES

Collision/reaction cell-ICP-MS



Simultaneous multi-element analysis?

Figure 1

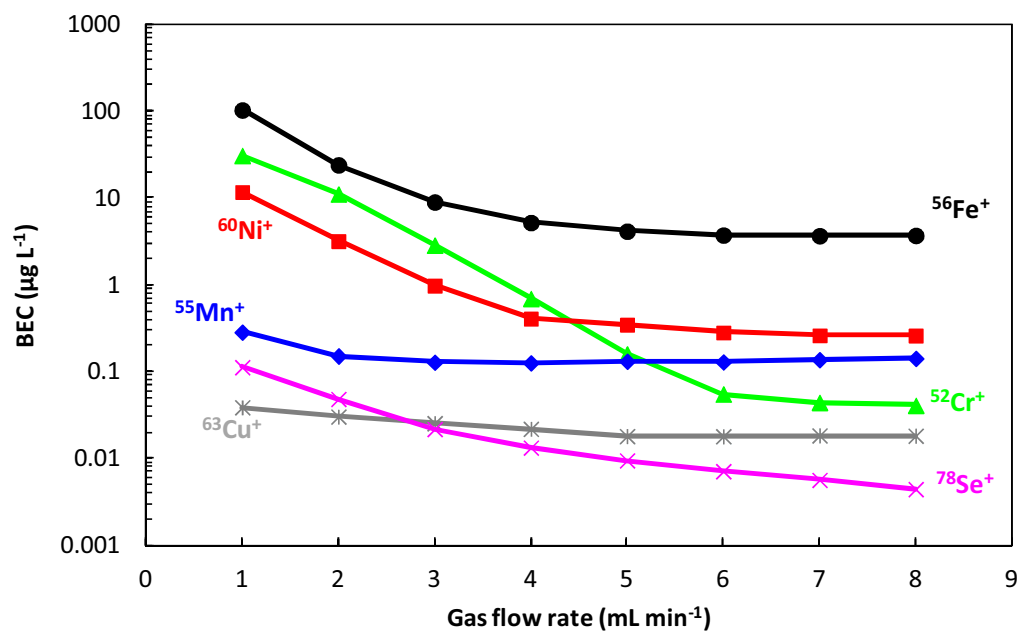
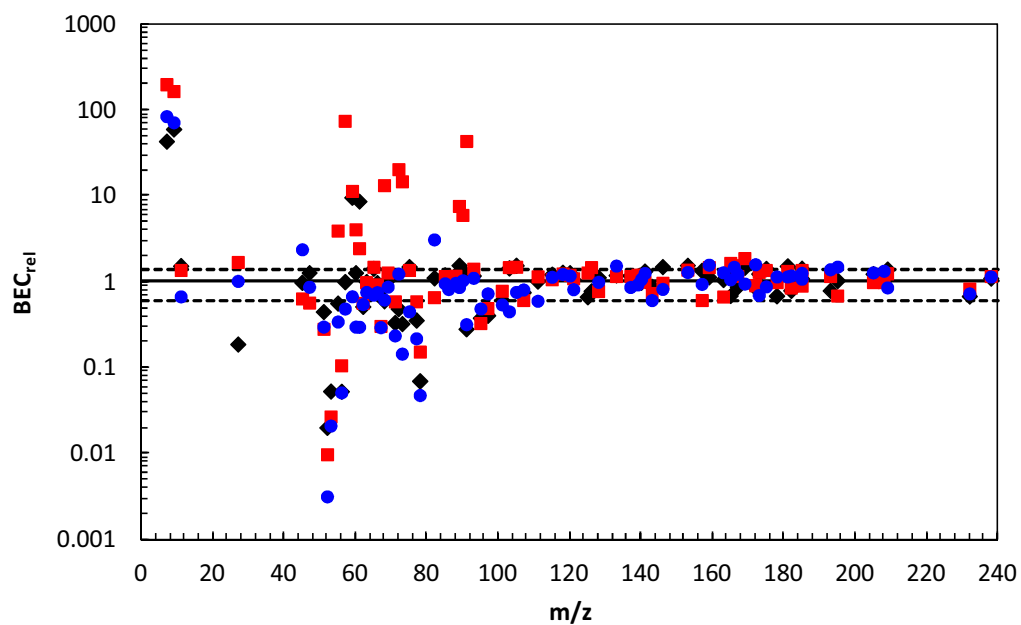
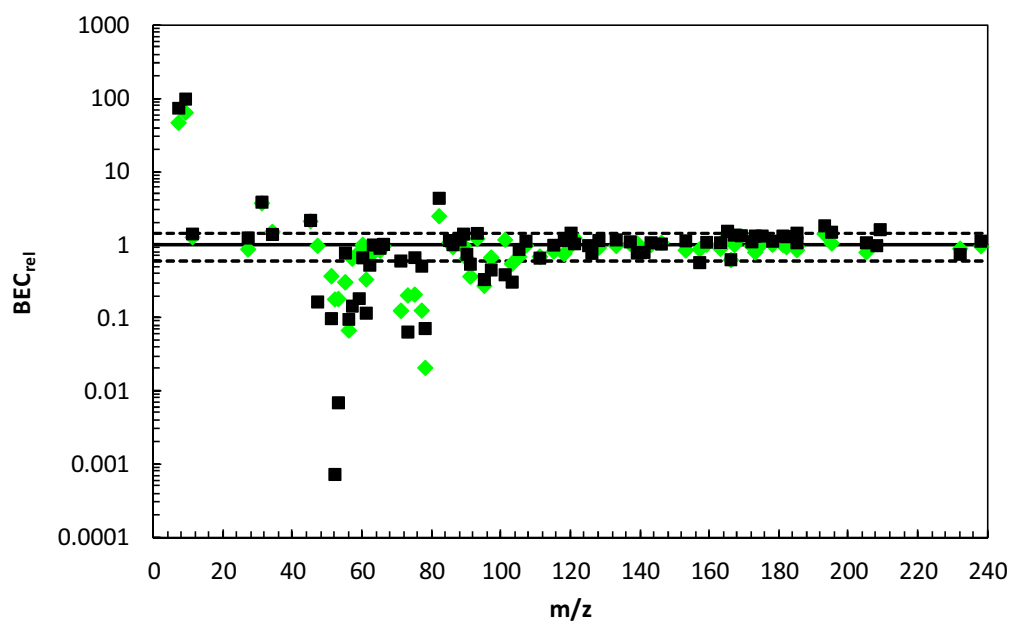


Figure 2



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Figure 3



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