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Inductively Coupled Plasma Mass Spectrometry

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-History of ICP-MS

-Presentation of the essential components of ICP-MS

-How to overcome analytical interferences

-How to correct for instrumental mass bias

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63 **Abstract**

64 Inductively coupled plasma mass spectrometry (ICP-MS) has grown tremendously since its
65 introduction in 1980, owing to its multi-element and isotopic analytical capability with flexible
66 sample introduction, high sensitivity, and fast sample throughput. In particular, integrating ICP
67 with a magnetic sector mass spectrometer and multiple collectors significantly improves the
68 precision of isotopic analysis for many elements that are difficult to measure with alternative
69 techniques. This chapter reviews the history of ICP-MS, its fundamental principles, and its
70 development for measuring concentrations and isotope ratios of elements prepared in aqueous
71 solutions. The review highlights critical technical advancements, novel approaches to address
72 spectral interferences, and the geochemical and cosmochemical applications that emerged from
73 these advances. Finally, potential avenues for future research are discussed.

74

75 **1 Introduction**

76 Over the past four decades, inductively coupled plasma mass spectrometry (ICP-MS) has
77 become the quintessential tool for analyzing the concentration and isotopic composition of most
78 elements across the Periodic Table. The ICP source features high efficiency for element ionization
79 with simple and flexible sample introduction (e.g., Houk et al., 1980; Houk 1986). The analytical
80 strength of ICP-MS is further enhanced by coupling with a multi-collector array for simultaneous
81 detection of different isotopes separated by a magnetic sector (i.e., MC-ICP-MS, Walder and
82 Freedman 1992; Walder et al., 1993), which provides sensitive and precise isotopic ratio
83 measurements at high sample throughput (e.g., Halliday et al., 1995; Hirata 1996; Vanhaecke et
84 al., 1996; Belshaw et al., 1998; Halliday et al., 1998; Maréchal et al., 1999).

85 The development of MC-ICP-MS has profoundly facilitated the isotopic measurement of
86 elements with high first ionization energies (Fig. 1) and low natural abundances, such as Hf (e.g.,
87 Blichert-Toft and Albarède 1997; Blichert-Toft et al., 1997), Zr (e.g., Schönbacher et al., 2004;
88 Inglis et al., 2018; Tompkins et al., 2020; He et al., 2021), W (e.g., Lee and Halliday 1995; Lee
89 and Halliday 1995; Yin et al., 2002; Kleine and Walker 2017), Fe (e.g., Belshaw et al., 2000; Zhu
90 et al., 2000; Weyer and Schwieters 2003; Dauphas et al., 2004), Ru (e.g., Becker et al., 2002; Hopp
91 et al., 2016), Os (e.g., Schoenberg et al., 2000; Norman et al., 2002; Nozaki et al., 2012; Ohta et
92 al., 2022), Ni (e.g., Moynier et al., 2007; Gueguen et al., 2013), Zn (e.g., Maréchal et al., 1999;
93 Luck et al., 2005), Cd (Wombacher et al., 2003; Cloquet et al., 2005; Ripperger and Rehkämper
94 2007), Hg (e.g., Evans et al., 2001; Lauretta et al., 2001; Chen et al., 2010; Geng et al., 2018), Si
95 (e.g., De La Rocha 2002; Cardinal et al., 2003; Georg et al., 2006; van den Boorn et al., 2006), Ge
96 (e.g., Hirata 1997; Luais et al., 2000; Rouxel et al., 2006; Siebert et al., 2006), Sn (e.g., Clayton et
97 al., 2002; Moynier et al., 2009; Balliana et al., 2013; Yamazaki et al., 2013; Creech et al., 2017;
98 Wang et al., 2017; She et al., 2023), Mo (e.g., Anbar et al., 2001; Siebert et al., 2001; Wieser et
99 al., 2007), Se (e.g., Rouxel et al., 2002; Elwaer and Hintelmann 2008; Zhu et al., 2008), and Te
100 (Lee and Halliday 1995; Fehr et al., 2004; Fornadel et al., 2014; Brennecka et al., 2017; Hellmann
101 et al., 2020).

102 MC-ICP-MS is the preferred method for isotopic analyses of elements with less than four
103 stable isotopes, for which instrumental isotope fractionation cannot be corrected by the
104 conventional double-spike method used in thermal ionization mass spectrometry (TIMS). A
105 critical limitation of TIMS is that the isotope ratio changes progressively as an analysis proceeds.
106 This fractionation occurs because samples are loaded as salts and heated on a metal filament, with
107 light isotopes being preferentially evaporated and ionized. In contrast, sample solutions are

108 continuously aspirated into the MC-ICP-MS during an analysis, leading to a relatively time-
109 independent instrumental isotope fractionation that can be corrected by external normalization.
110 Furthermore, MC-ICP-MS has a higher sample throughput than TIMS. These analytical
111 advantages of MC-ICP-MS have contributed significantly to the development of isotope
112 geochemistry of elements such as Li (e.g., Tomascak et al., 1999; Bryant et al., 2003; Liu et al.,
113 2023), K (e.g., Li et al., 2016; Wang and Jacobsen 2016; Hu et al., 2018; Morgan et al., 2018;
114 Moynier et al., 2021; Télouk et al., 2022; An et al., 2023), Rb (e.g., Waight et al., 2002; Nebel et
115 al., 2005; Nebel et al., 2011; Pringle and Moynier 2017; Nie and Dauphas 2019; Wang et al.,
116 2023), Mg (e.g., Galy et al., 2001; Teng et al., 2007; Young et al., 2009; Teng et al., 2010; Bizzarro
117 et al., 2011; Coath et al., 2017), Lu (e.g., Blichert-Toft et al., 1997; Vervoort et al., 2004), V (e.g.,
118 Nielsen et al., 2011; Prytulak et al., 2011; Nielsen et al., 2016; Wu et al., 2016), Cu (e.g., Maréchal
119 et al., 1999; Luck et al., 2003; Liu et al., 2014; Wang et al., 2022; Télouk et al., 2023; Luu et al.,
120 2024), B (e.g., Lécuyer et al., 2002; Aggarwal et al., 2003; Foster 2008; Louvat et al., 2011; Chen
121 et al., 2019), Ga (e.g., Yuan et al., 2016; Zhang et al., 2016; Kato et al., 2017), In (Liu et al., 2023),
122 Tl (e.g., Rehkämper and Halliday 1999; Nielsen et al., 2004), and Sb (e.g., Rouxel et al., 2003).

123 With the high-precision isotopic measurements of state-of-the-art MC-ICP-MS, non-
124 radiogenic isotope variations have been revealed for an increasing number of heavy elements, such
125 as Ti (Millet and Dauphas 2014; Millet et al., 2016; Greber et al., 2017; Deng et al., 2019; Aarons
126 et al., 2020; Deng et al., 2023), Fe (Poitrasson et al., 2004; Williams et al., 2004; Weyer and Ionov
127 2007; Teng et al., 2008; Sio et al., 2013), Sr (e.g., Fietzke and Eisenhauer 2006; Ohno and Hirata
128 2007; Moynier et al., 2010; Ma et al., 2013; Shalev et al., 2013), Nd (e.g., Ma et al., 2013; Ohno
129 and Hirata 2013; Saji et al., 2016), and U (e.g., Stirling et al., 2005; Rademacher et al., 2006;
130 Weyer et al., 2008; Brennecka et al., 2010; Hiess et al., 2012; Cheng et al., 2013; Tissot and

131 Dauphas 2015; Tissot et al., 2016). These findings have revolutionized the field of non-traditional
132 isotope geochemistry (see recent reviews by Johnson et al., 2004; Teng et al., 2017).

133 There are numerous reviews on various aspects of ICP-MS along with its progressive
134 development (e.g., Jarvis et al., 1992; Montaser 1998; Taylor 2001; Becker 2002; Albarède and
135 Beard 2004; De Groot 2004; Nelms 2005; Becker 2008; Hill 2008; Jakubowski et al., 2011;
136 Vanhaecke and Degryse 2012; Thomas 2013; Olesik 2014; Balcaen et al., 2015; Beauchemin
137 2020; Van Acker et al., 2023). A critical aspect of ICP analyses is the presence of three essential
138 components in the instrument: sample introduction, excitation, and detection. These components
139 have undergone several major developments in the various types of ICP analyses. The
140 characteristic feature of all ICP analyses is that samples are excited in the plasma to a very high
141 temperature and broken down into their constituent elements. The excited atoms are then separated
142 and detected in a mass spectrometer based on their mass-to-charge ratios. In mass spectrometry, it
143 is convenient to express the mass-to-charge ratio as m/z , which is the ratio between the mass (m)
144 of an ion in daltons and the number (z) of elementary charges (e) it carries. Because most ions
145 produced by Ar ICP carry a single positive charge, the m/z ratio is equivalent to the atomic (or
146 molecular) mass of an ion.

147 This chapter starts with a brief review of the history of ICP-MS, followed by a comprehensive
148 overview of the fundamental principles and recent developments in ICP-based analytical
149 techniques. The evolution of mass spectrometry for elemental concentration and isotopic ratio
150 analysis is discussed, including developing sample introduction systems, plasma interfaces, mass
151 analyzers, and highly sensitive detection techniques. In addition, novel approaches to overcoming
152 spectral interferences are presented. The discussion covers applications of ICP-MS in
153 cosmochemistry and geochemistry, and extends to future research directions.

154

155 **2 History of ICP-MS**

156 This section highlights significant milestones in the rich history of ICP. The development of
157 ICP began with the discovery of electric discharge in gases in the 1800s (e.g., Plucker and Hittorf
158 1865). Langmuir (1928) introduced the term "plasma" to describe the phenomenon of charged
159 particles carried in a neutral gaseous medium by analogy to electrolytes in blood plasma fluids.
160 Since then, it has evolved into a vital tool for breaking apart molecules and exciting the resultant
161 atoms to be analyzed [see the historical account by Ohls and Bogdain (2016)]. Initially, ICP
162 technology was developed to analyze solid samples (arc-spark) but was limited by ionization
163 efficiency and electrode contamination. In the 1940s, researchers developed electrodeless
164 discharges in high-frequency electromagnetic fields operated at atmospheric pressure (Babat
165 1947), which was the predecessor to modern ICP. The next innovation was the induction plasma
166 torch, capable of sustaining and thermally isolating a stable atmospheric plasma with flowing gas
167 streams inductively heated by a radio-frequency (RF) coil (Reed 1961a; b). Nevertheless, a major
168 obstacle to the application of ICP in analytical chemistry remained: developing an aqueous sample
169 introduction system for ICP-mass spectroscopy and spectrometry.

170 The application of ICP as an excitation source for atomic emission spectrometry (AES) was
171 pioneered by Greenfield et al. (1964) in the UK and Wendt and Fassel (1965) in the USA, utilizing
172 modified torch designs to introduce aerosols generated from liquid samples (Greenfield et al.,
173 1975; Fassel 1978). The Fassel torch is smaller than the Greenfield torch and has similar analytical
174 performance using lower gas flows and RF power; therefore, it has become widely adopted
175 (Greenfield 2000). Since ICP-AES is based on light emission and does not require a primary light
176 source, it is more convenient for multi-element analyses than atomic absorption spectroscopy

177 (AAS) and atomic fluorescence spectroscopy (AFS) (Fassel and Kniseley 1974). In addition, ICP
178 is a more effective excitation source than the combustion flame because of its high temperature,
179 allowing for elemental analyses with lower detection limits and greater dynamic ranges. Since its
180 inception, Ar plasma has become the standard ionization source for various ICP-based instruments.

181 ICP-MS evolved from ICP-OES (optical emission spectroscopy), with both methods sharing
182 similar sample introduction systems but different detector systems. In ICP-OES, the plasma excites
183 atoms to higher energy levels, and as they return to lower discrete energy levels, characteristic
184 optical emissions are measured with an optical spectrometer. The intensity of these emissions is
185 proportional to the concentration. In contrast, in ICP-MS, the plasma breaks apart molecules and
186 produces charged ions, which are separated by electromagnetic fields in a mass spectrometer and
187 detected as electric signals. A significant analytical difference between ICP-OES and ICP-MS is
188 that the former detects the total elemental concentration, whereas the latter detects individual
189 isotopes of each element. Furthermore, the detection limits of ICP-MS are generally several orders
190 of magnitude lower than for ICP-OES (Todolí 2019). Building on the pioneering work of Gray
191 (1974; 1975a; b), who successfully coupled a capillary-arc plasma with a mass spectrometer for
192 direct analyses of aqueous solutions introduced at atmospheric pressure, the first analytical ICP-
193 MS was presented by Houk et al. (1980). The high sensitivity of ICP-MS and its ability to measure
194 individual isotopes have led to the development of various types of mass analyzers for analyzing
195 the constituent masses of a variety of samples.

196 The magnetic sector ICP-MS and MC-ICP-MS are essential instruments for today's high-
197 precision elemental concentration and isotopic ratio measurements. Their working concepts can
198 be traced back to the end of the 19th century when physicists attempted to measure the m/z ratios
199 of cathode and anode rays within gas discharge tubes, which led to the discovery of electrons,

200 protons, and isotopes. Thomson (1897) and Wien (1898) independently observed the deflection of
201 cathode rays in an electrostatic field and identified them as streams of negatively charged particles
202 with weight, i.e., electrons. Wien (1898) also observed the deflection of collimated anode rays in
203 a strong magnetic field in the opposite direction to the cathode rays and found that these were
204 positively charged particles with the mass of hydrogen atoms, i.e., protons. Building on these
205 findings, J. J. Thomson designed the archetypal mass spectrograph that deflected ions by parallel
206 magnetic and electric fields and imaged their parabolic trajectories on a photographic plate. Using
207 this parabola spectrograph, Thomson (1913) provided the first proof of stable isotopes (^{20}Ne and
208 ^{22}Ne). This discovery motivated ongoing efforts to determine the exact atomic masses of elements
209 and to develop improved analytical instruments for quantitative isotopic analyses, paving the way
210 for the development of modern MC-ICP-MS.

211 MC-ICP-MS was invented to overcome the limitations of high-precision isotopic analyses
212 using existing mass spectrometry techniques. Substituting the thermal ionization source (< 2800
213 K) with a more energetic ICP source (5000-10,000 K) substantially improves the ionization
214 efficiency for elements with high first ionization energies (Fig. 1). Also, instrumental isotope
215 fractionation is relatively stable during MC-ICP-MS analysis. Source instability, which is the
216 primary limiting factor for high-precision isotopic measurements with ICP instruments, is
217 overcome by using a magnetic sector to spatially separate ion beams according to their m/z ratios
218 and direct them into a set of designated collectors. This capability of simultaneous analyses of
219 multiple isotopes over a narrow mass range is the primary purpose of MC-ICP-MS, which
220 contrasts with traditional ICP-MS techniques that focus on multi-element analyses by sequentially
221 detecting individual ion beams rapidly scanned across a wide mass range. The original MC-ICP-
222 MS, known as the Plasma 54, was a hybrid between the VG PlasmaTrace magnetic sector ICP-

223 MS and the Sector 54 TIMS. Analyses of U and Pb isotopic ratios with this instrument yielded
224 accuracy and precision similar to those obtained using TIMS (Walder and Freedman 1992). Since
225 then, MC-ICP-MS instruments have been advancing rapidly to achieve unprecedented precision,
226 and ICP-MS has become a leading technique for elemental and isotopic analyses.

227

228 **3 Primary components of ICP-MS**

229 ICP-MS has undergone significant development in its primary components, leading to the
230 current state-of-the-art systems. These components are as follows (Fig. 2):

231 (1) a sample introduction system that brings a solution or solid sample to the ICP to break it
232 down into ionizable atoms

233 (2) an ion source that forms ions and accelerates the positively charged particles

234 (3) an interface that samples ions formed at atmospheric pressure into the vacuum of the mass
235 spectrometer

236 (4) a mass analyzer that sorts ions by their m/z ratios

237 (5) an ion detection system that produces electrical signals

238 **3.1 Sample introduction**

239 ICP-based analyses produce free atoms that can be readily excited and ionized by the plasma.
240 Initially, samples must be effectively introduced to the plasma. Solution nebulization is most
241 commonly used, where a liquid sample is converted into a fine aerosol using a nebulizer (from
242 Latin *nebula*, meaning "mist"). In contrast, laser ablation is used for *in situ* analysis of solid
243 samples, as discussed in another chapter of this volume. This chapter mainly concerns the solution
244 nebulization method that delivers a fine aerosol to the plasma. Since only a few percent of an

245 aspirated sample eventually reaches the plasma (Gray 1975), efficient and consistent sample
246 introduction is critical for reproducible signal output and the stable operation of the plasma.

247 **3.1.1 Nebulization**

248 Most ICP-based analyses use a pneumatic nebulizer that passes a high-speed gas through a
249 converging nozzle to break liquids into aerosols (e.g., Sharp 1988; Todoli and Mermet 2011).
250 Liquid samples are aspirated by a sampling probe connected to a fine capillary in the center of the
251 nebulizer. The nebulizer is typically fed with a stream of compressed argon gas that accelerates to
252 sonic velocity when it emerges from the nebulizer nozzle, providing the mechanical force to
253 disperse the liquid and form an aerosol. The gas is commonly supplied in the outer capillary
254 concentric to the central sample capillary (concentric nebulizer, Fig. 3A) (e.g., Meinhard 1976;
255 Meinhard 1979) or at a right angle to the sample capillary by a second gas capillary (cross-flow
256 nebulizer, Fig. 3B) (e.g., Valente and Schrenk 1970; Kniseley et al., 1974). Concentric nebulizers
257 have fine-bore capillaries that facilitate the kinetic energy transfer between gas and liquid. They
258 create a fine aerosol within a narrow size range, offering superior sensitivity and stability for
259 routine analyses of clean solutions. In comparison, cross-flow nebulizers allow wider liquid
260 capillaries and are preferred for samples containing undissolved particles or high levels of heavy
261 element matrices. Parallel path nebulizers are also used for samples with larger particles and high
262 salt contents, whereby a liquid sample is pumped parallel to the nebulizer gas stream, thereby being
263 entrained into the gas flow and forming an aerosol.

264 The development of low-flow nebulizers has facilitated effective ionization using a
265 significantly reduced sample volume (Olesik et al., 1994; Vanhaecke et al., 1996; Boulyga and
266 Becker 2001; Todolí and Mermet 2006). For instance, a 50- μ L/min nebulizer with 50% efficiency
267 consumes 20-40 times less sample than a standard flow nebulizer (1-2 mL/min) with \leq 5%

268 efficiency, while sensitivity is only reduced by a factor of ≤ 2 (Fig. 3C). The increased efficiency
269 of sample transport and fragmentation is likely due to increased kinetic energy to liquid ratio and
270 decreased droplet coalescence at reduced sample uptake rates (Meinhard 1979; Todoli and Mermet
271 2011; Olesik et al., 2021). These micro-nebulizers enable the analysis of samples of limited size
272 and contribute to a more robust plasma by reducing solvent loading to the plasma and preventing
273 the formation of solvent-related interferences.

274 Nebulization can proceed with or without external pumping, depending on the nebulizer and
275 ICP-MS system in use. While self-aspiration occurs due to the pressure drop created as argon flows
276 through the nebulizer nozzle and is accelerated (Venturi effect), a peristaltic pump is recommended
277 for elemental analyses in ICP-MS to ensure a constant, regulated sample flow and to minimize the
278 impact of sample viscosity on the uptake rate. In contrast, isotopic ratio analyses in MC-ICP-MS
279 usually do not require a peristaltic pump for sample uptake, as the elements of interest are analyzed
280 in dilute concentrations with little differences in viscosity. This direct sample uptake without a
281 peristaltic pump shortens the sample path to the nebulizer and reduces sample consumption. In
282 addition, sample contamination is minimized as interactions with the pump tubing are avoided,
283 which is beneficial for isotope analysis. However, if no peristaltic pump is used, keeping the liquid
284 surfaces of the sample and standard solutions at the same height is crucial to avoiding differential
285 uptake rates between analyses.

286 **3.1.2 Conventional sample introduction systems**

287 Depending on analytical needs, the nebulizer is fitted onto a spray chamber (Fig. 4), a
288 desolvation device (Fig. 5), or it can be mounted directly on the torch, corresponding to three types
289 of sample introduction systems: "wet" plasma introduction, "dry" plasma introduction, and direct
290 injection nebulization (DIN). "Wet" plasma introduction is the simplest and most compact, using

291 a spray chamber to filter large droplets. This sample introduction typically provides the best
292 stability and precision and is preferred when there is sufficient sample. In comparison, "dry"
293 plasma introduction uses a semi-permeable heated Teflon® membrane to remove most of the
294 solvent, thereby offering substantially higher sensitivity than the "wet" plasma introduction (Fig.
295 6). It is preferred when the analyte is limited or if solvent-related spectral interferences occur.
296 Finally, the less common DIN requires a specially designed nebulizer and generally provides
297 sensitivity between "wet" and "dry" plasma introduction (Fig. 6).

298 **3.1.2.1 "Wet" plasma introduction using a spray chamber**

299 The aerosols formed by a pneumatic nebulizer have a range of diameters, and only those
300 smaller than $\sim 10 \mu\text{m}$ can be efficiently ionized by the plasma (e.g., Olesik 2014). This size limit
301 occurs because the evaporation rate of solvent in a droplet increases with its surface area to volume
302 ratio. Larger droplets that are not entirely vaporized upon entering the plasma can significantly
303 cool the plasma or even cause it to extinguish. The stability of the plasma can be improved by
304 using a spray chamber to condense larger aerosol particles; however, this also removes about 95%
305 of the liquid sample taken up by the nebulizer.

306 The two most common designs of spray chambers are the cyclonic type and the Scott type;
307 both can have baffles that serve as a secondary droplet size separator to further reduce aerosol size
308 distribution (Fig. 4). When passing through a spray chamber, the fine aerosol travels in the
309 streamline of the carrier gas. In contrast, the larger droplets, due to their greater size and
310 momentum, impinge on the spray chamber wall or the baffle and form a condensate, which is
311 pumped out to the waste. A cyclonic spray chamber separates larger liquid droplets by centrifugal
312 force during the angular flow of the sample aerosols. In comparison, a double-pass Scott-type
313 spray chamber selectively funnels the small droplets into a central tube, whereas the larger droplets

314 will condense and divert to the drain. Spray chambers are typically cooled thermoelectrically
315 (Peltier cell) to minimize water vapor entering the plasma and forming associated oxides. The
316 cooling device also stabilizes the spray chamber temperature, thereby reducing temperature-related
317 signal drift.

318 Both nebulizers and spray chambers can be manufactured from glass, quartz, or Teflon®,
319 depending on their intended use. Quartz nebulizers and spray chambers have the longest lifespan
320 and are recommended for clean samples with low salt contents. On the other hand, Teflon®
321 nebulizers and spray chambers resist hydrofluoric acid (HF) but are more expensive and softer
322 than quartz ones.

323 **3.1.2.2 "Dry" plasma introduction using desolvation membrane**

324 In contrast to "wet" plasma introduction, where solvent vapors condense on the cooled spray
325 chamber walls, desolvation can be enhanced by heating the spray chamber with a downstream
326 mechanism to remove solvent vapors (e.g., a membrane desolvator or cold condenser). In a typical
327 desolvation nebulizer system, the sample aerosol is transported into a heated, semi-permeable
328 Teflon® membrane, through which solvent vapors can pass freely and be removed by an external
329 gas flow (Fig. 5). The desolvated sample contained in the membrane is carried into the plasma.
330 Inlet gas is preheated and directed at the chamber walls to prevent condensation of sample aerosols.
331 For applications unaffected by nitrogen-based interferences, a small amount of N₂ can be blended
332 into argon to enhance sensitivity and reduce oxide formation (see Section "Mixed-gas plasma").

333 Several desolvation nebulizer systems are commercially available (Fig. 5). The DSN-100 from
334 Nu Instruments is the only one that works with glass instead of Teflon® nebulizers, but its
335 production has been discontinued. Teledyne CETAC produces the Aridus series (Aridus, Aridus
336 II, and Aridus 3), with the Aridus 3 featuring software control of gas flow and temperature.

337 Elemental Scientific Inc. (ESI) offers a selection of systems for specific applications, such as Apex
338 Q (Quartz flow path), Apex IR (for Isotope Ratio analysis), and Apex HF (for samples containing
339 HF). The latest software-controlled Apex Omega combines a heated cyclonic spray chamber, a
340 multi-pass Peltier-cooled condenser, and a heated membrane desolvator to achieve multi-stage
341 solvent vapor removal. This system improves sample introduction efficiency and sensitivity, which
342 is particularly useful for samples that contain high levels of dissolved solids or that are difficult to
343 analyze by conventional nebulization methods.

344 **3.1.2.3 Direct injection nebulizer (DIN)**

345 Some elements (e.g., B, Hg, Mo, Si, Sn, W, Zn, and Zr) tend to be absorbed in the introduction
346 system and released during subsequent runs, causing memory effects and inaccurate analyses. To
347 alleviate this carry-over effect, DIN has been developed, whereby a micro-concentric nebulizer is
348 mounted at the base of the plasma torch so that the aerosol sprays directly into the plasma without
349 passing through and contacting a spray chamber. This design not only reduces memory effects but
350 also achieves ~ 100% sample transport efficiency to the plasma, which is a significant
351 improvement over the 1 - 2% efficiency of conventional nebulizer-spray chamber arrangements
352 (Browner and Boorn 1984). The DIN was first used in single-collector ICP-MS and ICP-AES for
353 elemental analyses (LaFreniere et al., 1985; LaFreniere et al., 1987), and it has later been employed
354 for isotopic measurements using MC-ICP-MS (e.g., B, Smith et al., 1991; Louvat et al., 2011).

355 **3.1.3 Sample introduction accessory: Hydride generation system**

356 Hydride generation (HG) is an effective technique for introducing As, Bi, Ge, Pb, Sb, Se, Sn,
357 Te, and Hg (e.g., Thompson et al., 1978a; b; Godden and Thomerson 1980; Date and Gray 1983;
358 Powell et al., 1986; Wang et al., 1988; Dean et al., 1990). These elements are difficult to detect
359 using conventional nebulization due to their low natural abundances, high first ionization energies

360 (Fig. 1), and widespread matrix- or solvent-related interferences. In an HG system, the liquid
361 sample is introduced using a peristaltic pump and mixed online with a strong acid (e.g., HCl or
362 HNO₃). Further down-line, the acidified sample is mixed with a reducing agent (e.g., NaBH₄
363 stabilized with NaOH), converting the analyte elements to volatile species that evolve from the
364 bulk liquid and are entrained by the argon stream into the torch. A spray chamber is often used as
365 a gas-liquid separator to improve plasma stability and detection limits, and to allow the
366 simultaneous detection of non-hydride forming elements (e.g., Huang et al., 1987; Huang et al.,
367 1988; Heitkemper and Caruso 1990; Zhang and Combs 1996).

368 This technique offers two advantages over standard nebulization. First, the generation and
369 transport of volatile analytes can approach 100% efficiency, which increases sensitivity by two
370 orders of magnitude. Second, most matrix effects and spectral interferences (e.g., ⁴⁰Ar³⁵Cl⁺ on
371 ⁷⁵As⁺) are eliminated prior to detection by separating the volatile analytes from the bulk liquid
372 containing sample matrices, solvents, and reaction solutions. The coupling of HG with MC-ICP-
373 MS is particularly beneficial to isotopic analyses, as the HG settings can be optimized for a single
374 element. High-precision isotopic analyses have been achieved for Se (e.g., Rouxel et al., 2002;
375 Ellis et al., 2003; Kurzawa et al., 2017; Stüeken 2017), Te (e.g., Brennecka et al., 2017; Wasserman
376 and Johnson 2020), Ge (e.g., Escoube et al., 2012; Karasiński et al., 2021), and Hg (e.g., Geng et
377 al., 2018; Moynier et al., 2020) using as little as nanograms of samples.

378 **3.2 The ICP discharge**

379 Sample aerosols are carried by gas flowing into the ICP torch that sustains the plasma. The
380 torch typically comprises three concentric quartz tubes (Fig. 7), which withstand the significant
381 temperature gradient toward the plasma owing to the low thermal expansion coefficient and
382 thermal conductivity of quartz (e.g., Reed 1961; Greenfield et al., 1964; Fassel and Kniseley 1974).

383 A fast stream of *cooling gas* (12-18 L/min) and a slower stream of *auxiliary gas* (~ 1 L/min) spiral
384 around the outer and middle tube, respectively, which sustain the plasma, centering and
385 constricting it radially to prevent the torch from melting. These vortex gas flows create a low-
386 pressure central channel for sample injection by the *nebulizer gas* (~ 1 L/min). The three tubes are
387 usually assembled as one piece. Alternatively, the sample injector can be a demountable piece for
388 applications requiring a specific bore size, configuration, or more corrosive-resistant materials
389 (e.g., sapphire, alumina, platinum, and ceramic).

390 Argon is considered the most practical gas for generating and sustaining an ICP at atmospheric
391 pressure for the following reasons. First, argon is chemically inert because it has a completely
392 filled valence shell that stabilizes its electronic configuration without bonding to other atoms.
393 Second, a monatomic gas like argon can only store heat as translational kinetic energy, unlike
394 diatomic gases (e.g., N₂ and O₂), which may also store energy through rotation and vibration at
395 ionization temperatures. Hence, argon absorbs less heat per degree of temperature rise than
396 diatomic gases. Third, argon is the most abundant among the noble gases. It is heavier than air and
397 accumulates in the atmosphere. Therefore, it is less expensive to purify in bulk than neon and
398 helium. Last, the lower ionization energy of argon relative to neon and helium requires a less
399 powerful system to sustain an Ar plasma (Fig. 1A).

400 Argon ICP is a weakly-ionized plasma (~ 0.1%, Niu and Houk 1996) sustained by converting
401 the electrical energy from an RF generator into gas enthalpy via inductive heating (Fig. 7).
402 Coupling is achieved by sending an oscillating RF signal (typically 0.5-1.5 kW at 27.12 or 40.68
403 MHz) through a copper coil (2-3 turns) encircling the torch exit, which induces a poloidal
404 electromagnetic field oscillating at the same frequency (e.g., Todoli 2019). When the gas in the
405 coil space is seeded with electrons, conventionally by a high-voltage spark from a Tesla coil, some

406 gas atoms are ionized on collisions. The charged particles are accelerated by the RF magnetic field
407 and set to move in closed circular paths, leading to a cascade propagation of collisional ionizations
408 almost instantaneously and heating of the plasma once initiated.

409 Toroidal plasma is a robust source for excitation and ionization. Critically, sample aerosols are
410 able to retain their compositional integrity due to limited mixing with the annular plasma. Sample
411 aerosols are injected through the central channel of the plasma, traveling an extended time (1-2
412 ms) in the flame-like plasma with minimal disturbance to the induction region. Plasma
413 temperatures can reach 8000 to 10000 K in the induction zone and are slightly lower (5000-7000
414 K) in the plasma tail (analytical zone). The high temperature evaporates aqueous solvents from the
415 analyte salt, breaking down constituent ionic bonds and converting the gaseous atoms into positive
416 ions. Ionization occurs via several pathways. Thermal ionization occurs during collisional energy
417 transfer between atoms, ions, and electrons (e.g., $\text{Ar} + e^- \rightarrow \text{Ar}^+ + 2e^-$). Penning ionization occurs
418 when ground-state atoms interact with metastable Ar species ($\text{Ar}^m + \text{M} \rightarrow \text{Ar} + \text{M}^+ + e^-$). Charge
419 transfer occurs when electrons are transferred between ions and atoms ($\text{Ar}^+ + \text{M} \rightarrow \text{Ar} + \text{M}^+$).

420 Argon ICP primarily produces singly charged ions because argon has a first ionization energy
421 (15.8 eV) that lies between the first and second ionization energies of most elements (Fig. 1A).
422 According to Houk (1986), elements with first ionization energies lower than 8 eV achieve over
423 90% ionization, and alkali and alkaline earth elements are the easiest to ionize. Furthermore, the
424 alkaline earth elements and rare earth elements (REEs) have sufficiently low second ionization
425 energies that doubly charged ions may occur (e.g., Ca^{2+} , Sr^{2+} , and Ba^{2+}) (Fig. 1B). Non-metals,
426 metalloids, and certain metals have lower ionization efficiencies. Elements with first ionization
427 energies of 8-9 eV (B, Si, Pd, Cd, Os, Ir, and Pt) reach 93-58% ionization, of 9-10 eV (Be, Zn, As,

428 Se, Te, and Au) reach 75-33% ionization, and of 10-11 eV (P, S, I, and Hg) reach 38-14%
429 ionization, respectively. Only a few percent are ionized for elements such as Br and Xe.

430 **3.3 The ICP-MS interface**

431 The interface region extracts ions formed in the ICP (~ 1000 mbar) into a differentially pumped
432 vacuum system (10^{-5} to 10^{-10} mbar) in which the mass spectrometer is contained (Fig. 8A). An
433 atmospheric-pressure ion source offers the flexibility of switching between different introduction
434 systems and using alternative gases to adapt to specific application needs. By contrast, mass
435 spectrometers operate under high vacuum, allowing the sampled ions to reach the detectors with
436 minimal reaction, neutralization, scattering, or fragmentation due to collisions with other ions or
437 gas molecules. A well-maintained vacuum is vital for accurate and precise measurements. It
438 minimizes spectral interferences from air, water, gas molecules, or other contaminants. It also
439 improves peak shape by reducing ion scattering and background noise, and prevents arcing in the
440 high electric potential field. The substantial pressure and temperature gradients across the interface
441 present a fundamental challenge for its design, and high ion transmission into the mass
442 spectrometer has to be achieved without compromising its high vacuum.

443 The concept of mass spectrometric sampling of plasma ions stems from the use of supersonic
444 free jets to form molecular beams. This concept was established by the theoretical work of Owen
445 and Thornhill (1948) and Kantrowitz and Grey (1951) and was experimentally demonstrated by
446 Johnson (1927; 1928), Kistiakowsky and Slichter (1951), and Becker and Bier (1954). By
447 admitting gas into a low-pressure chamber through a small nozzle, the emerging stream undergoes
448 a near-adiabatic, enthalpy-driven expansion. During this expansion, a substantial portion of the
449 random thermal motion upstream of the nozzle is converted into an ordered motion with a narrow
450 velocity distribution, forming a high-intensity, directed, and nearly collisionless beam. This nozzle

451 expansion is accompanied by rapid rarefaction and cooling of the admitted gas stream; therefore,
452 it is an ideal mechanism for interfacing a continuum gas flow from the high-temperature,
453 atmospheric ICP source with a mass spectrometer kept under vacuum.

454 Following the practice of sampling flames (Hayhurst et al., 1971), a conical metal duct ("cone")
455 with a circular orifice in its tip is typically used for plasma extraction. It allows the plasma gas to
456 sweep smoothly over its surface with little disturbance from the back pressure, and the central flow
457 passing through the tip to expand freely inside the cone into the first vacuum stage of the
458 instrument. The cone is supported on a grounded, water-cooled mount to prevent melting by the
459 plasma. When the plasma impinges on the cone, a boundary layer of cool gas forms over the cone
460 (Hayhurst and Kittelson 1977), where unwanted chemical and physical interactions may occur to
461 alter the relative populations of the plasma constituents. In addition, a thin electron-poor sheath
462 may develop around the sampling orifice as electrons have a smaller mass and greater velocity
463 than cations and, therefore, have a higher frequency of striking the cone to be neutralized (e.g.,
464 Chambers et al., 1991; Niu and Houk 1996). It is essential to prevent significant charge separation
465 during ion sampling and to ensure the integrity of the sampled plasma.

466 The diameter of the sampling orifice is a limiting factor for a representative ion sampling. The
467 orifice should be sufficiently large so that a fraction of the bulk plasma can flow through it in an
468 ordered motion as a continuum. The flow regime is determined by the Knudsen number (K_n),
469 which is the ratio of the mean free path (λ) of the plasma gas at the throat of the sampling orifice
470 to its diameter (D_0). Continuum flow occurs if $K_n < 0.01$, which means that D_0 should be at least
471 100λ wide. The mean free path ($\lambda = 1/n\sigma$) of a conventional Ar ICP is less than 2×10^{-3} mm,
472 assuming a number density of the gas $n = 1.5 \times 10^{18}/\text{cm}^3$ and an Ar collision cross section $\sigma = 5$
473 $\times 10^{-15} \text{ cm}^2$ (Douglas and Tanner 1998). The sampling diameter also needs to be substantially

474 larger than the Debye length of the ICP (λ_D), estimated to be 10^{-3} to 10^{-4} mm (Douglas and Tanner
475 1998), to shield the charged plasma species from external fields and avoid significant charge
476 separation. Given these considerations, an orifice wider than 0.2 mm is preferable (Date and Gray
477 1983; Gray and Date 1983).

478 Early efforts to extract ions from the plasma relied on a high-capacity pump to maintain a low
479 background pressure ($< 10^{-3}$ Torr) in the first vacuum stage (e.g., Gray 1975a; b; Houk et al., 1980),
480 similar to the Fenn-type expansion used in molecular beam studies (Fenn 2000). Nevertheless, the
481 size of the sampling orifice used in these earlier studies (0.050-0.125 mm) was limited by the mass
482 throughput the oil diffusion pumps could handle and the frequent occurrence of secondary
483 discharge when the sampler orifice exceeded 0.1 mm (e.g., Gray and Date 1981; Houk et al., 1981).
484 Due to the weaker suction of a smaller orifice, the sampled gas has to traverse a thicker boundary
485 layer (Hayhurst and Kittelson 1977). This boundary layer sampling was prone to orifice clogging,
486 undesirable oxide formation, and ion-molecule reactions (e.g., Date and Gray 1983a; b).

487 To overcome the practical limitations of boundary layer sampling, an alternative sampler-
488 skimmer interface has been developed for continuum sampling from the bulk plasma (Douglas and
489 French 1981; Date and Gray 1983; Douglas et al., 1983). This sampling arrangement utilizes the
490 Campargue-type expansion (Campargue 1964; 1984), by which the atmospheric plasma gas
491 propagates supersonically into a relatively high background pressure (a few Torr), forming a
492 concentric barrel shock that terminates at a perpendicular shock wave (i.e., the Mach disk) (Fig.
493 8B). The core of the supersonic expansion is effectively shielded from the background gas by the
494 shock-wave structure (i.e., zone of silence), and the center-line flow is skimmed into the second
495 vacuum stage at a much lower pressure (10^{-3} to 10^{-4} Torr). A mechanical pump is sufficient for
496 evacuating the region between the sampler and skimmer cones. The relatively high background

497 pressure in this region permits the use of a larger orifice (~ 0.41 to 1 mm diameter) to sample the
498 bulk plasma with an increased ion flux, which improves the detection limits and dynamic range of
499 the ICP-MS while reducing oxide formation and salt deposition at the orifice (Douglas and Houk
500 1985). The impedance matching network and tank circuit were modified accordingly to prevent
501 the occurrence of secondary discharges (Douglas and French 1986). This improved interface
502 design eventually led to the introduction of the first commercial ICP-MS by PerkinElmer-SCIEX
503 in 1983.

504 A typical interface of modern ICP-MS is shown in Fig. 8B), and the gas dynamics of the
505 interface is detailed by Douglas and French (1988). For sampling an Ar ICP with a gas kinetic
506 temperature of 6000 K, as the plasma is drawn adiabatically through the sampling orifice (diameter
507 $D_0 \sim 1$ mm), the axial flow accelerates to local speed of sound ($a_0 = (\gamma k T_0 / m)^{0.5} = 1.4 \times 10^5$ cm/s)
508 at a distance of $x = 0.5 D_0$ downstream of the sampler, and reaches terminal speed ($u = (5 k T_0 / m)^{0.5}$
509 $= 2.5 \times 10^5$ cm/s) at $x \geq 2 D_0$. Assuming the plasma expands from atmospheric pressure (P_0) into a
510 background pressure (P_1) of ~ 2 Torr, the shock wave terminates at the Mach disk located at $x_m =$
511 $0.67 D_0 (P_0 / P_1)^{0.5} = 13$ mm. The skimmer is typically placed before the Mach disk at $\sim 2/3 x_m$ to
512 allow high ion transmission while minimizing background gas penetration into the supersonic jet,
513 corresponding to a sampler-skimmer spacing of 7-8 mm and a travel time of about 3 μ s. This short
514 transit time limits the occurrence of ion-molecule chemistry. In addition, while electron density
515 decreases with $1/x^2$, resulting in an increase in λ_D from $\sim 10^{-4}$ mm at the sampler to 10^{-3} - 10^{-2} mm
516 at the skimmer tip, λ_D remains much smaller than a typical skimmer orifice (0.4-0.8 mm diameter).
517 Therefore, the ion population sampled through the sampler and skimmer resembles that in the
518 plasma source.

519 Downstream of the skimmer orifice, the electron density continues to decrease to the extent
520 that λ_D becomes significant for charge separation (Niu and Houk 1994). With their high mobility,
521 electrons diffuse readily to the inner wall of the skimmer cone where an electron sheath forms.
522 The initially quasi-neutral beam takes on a positive net charge and expands radially (defocuses)
523 due to coulomb repulsion. The heavier ions, which have greater momentums, are repelled less than
524 the lighter ions and are transmitted preferentially. Thus, analyte transmission efficiency is affected
525 by the concentration and atomic mass of the constituent elements, and the isotopic composition
526 measured for a given element is likely to be heavier than the true isotope ratio. This mass
527 discrimination due to space charge accounts for many aspects of the matrix effects (e.g., Gillson
528 et al., 1988; Tanner 1992) and must be corrected appropriately (see Section “Instrumental isotope
529 fractionation”). To mitigate space charge and matrix effects, a triple-cone interface has been
530 developed, which produces a less dispersed ion beam with a reduced ion current flux through the
531 interface orifices (Tanner et al., 1994a; b).

532 Ions emerging from the interface have divergent trajectories along the slope of the skimmer
533 cone due to space charge effects and the variable ion kinetic energies acquired during the
534 expansion-driven acceleration. The Ar flow and entrained ionized species accelerate to a similar
535 velocity of ~ 2500 m/s, resulting in a mass-dependent spread in ion kinetic energy from 0.5 to 10
536 eV for a mass range from Li to U. The ion kinetic energies may be increased by an additional
537 voltage offset of 10 to 20 eV between the plasma and the sampler cone due to capacitive coupling
538 between the induction coil and the plasma (Douglas and French 1986). This wide dispersion of ion
539 kinetic energy creates problems for ion focusing and reduces the achievable mass resolution of a
540 mass analyzer. These detrimental effects can be reduced by accelerating the positive ions to a
541 suitable velocity to travel toward the detection system. A high acceleration voltage (typically 4000-

542 10,000 V) is applied in magnetic sector-ICP-MS to dilute the initial ion kinetic energy spread,
543 whereas a smaller acceleration voltage (~ 300 V) is used in quadrupole-ICP-MS to allow ions to
544 pass sufficient RF cycles for mass selection.

545 The sampler and skimmer cones are commonly made from nickel, a durable metal suitable for
546 most samples, while platinum cones are preferred for more corrosive samples or rinsing solutions.
547 The geometry of the cone has a crucial impact on ion transmission, space charge effects, and the
548 introduction of sample matrices into the mass spectrometer. Notably, "wet" and "dry" sample
549 introduction systems are paired with separate sets of cones, which vary by manufacturer and can
550 be tailored to specific analytical requirements. For example, a Jet sampler cone with a slightly
551 wider orifice and an X-skimmer cone with a trumpet-shaped entrance can be used for the Neptune
552 Plus MC-ICP-MS to increase sensitivity by 5-10 times (e.g., Newman 2012; He et al., 2016).

553 **3.4 Ion optics**

554 The ion beam leaves the interface with a defocused circular profile. It then passes through an
555 ion-focusing system to be reshaped into a narrow rectangular profile while being directed toward
556 the detectors. This focusing system consists of a series of metal slits, plates, barrels, and cylinders.
557 By varying the polarity and strength of applied voltages, the ion trajectory and the degree of
558 focusing can be adjusted. A circular or conical extraction lens is placed after the skimmer cone to
559 extract positive ions while rejecting electrons, neutral atoms, and molecules as much as possible.
560 This lens significantly improves the transmission efficiency of low-mass elements that are displaced
561 further away from the centerline of the ion beam by the heavier elements. Succeeding lenses adjust
562 the ion beam in vertical and horizontal directions, refining its focus, alignment, and trajectory.
563 Focusing the ion beam precisely through these lenses reduces ion loss and increases analytical
564 sensitivity.

565 For instruments that employ a multi-collector block with fixed physical spacing, additional
566 zoom lenses are placed between the magnet and the collector block to adjust the mass dispersion
567 between ion beams, thereby directing them into designated collectors. As an illustration, Nu
568 instruments use a magnet with an effective radius of ~ 500 mm. It has a dispersion for Nd isotopes
569 of 3.4 mm per amu, which is set to be the fixed spacing between adjacent collectors. This spacing
570 is wider than the dispersion between adjacent isotopes of elements heavier than Nd (e.g., U), and
571 a negative quadratic voltage is applied to magnify the ion beam image at the collectors (Fig. 9A).
572 For lighter elements such as Sr, the magnet leads to a dispersion of ~ 5.8 mm between its isotopes
573 (Fig. 9B). While applying a positive quadratic voltage can demagnify the ion beam image into
574 adjacent collectors, this may lead to significant distortions. Alternatively, the dispersion is widened
575 to 6.8 mm by applying a negative quadratic voltage so that different Sr isotopes can be directed
576 into every other collector with appropriate peak shapes (Fig. 9C).

577 **3.5 Mass analyzer**

578 The mass analyzer is the central component of an ICP-MS; it uses magnetic and electric fields
579 to separate ions based on their m/z ratios. Ions with different m/z ratios are separated according to
580 their kinetic energies, momentums, and velocities. These properties form the basis for designing
581 various mass analyzers, with magnetic sector, quadrupole mass filter, and time-of-flight (TOF)
582 analyzers being the most prevalent in ICP-MS. They use different mass separation mechanisms,
583 which lead to their characteristic resolution and detection capabilities.

584 **3.5.1 Critical characteristics of mass analyzers**

585 **3.5.1.1 Mass resolution**

586 The resolution of a mass spectrometer defines its ability to distinguish ions with small mass
587 differences. Resolution is typically quantified by the ratio of the mass being analyzed (m) to the

588 smallest increment in mass (Δm), i.e., $m/\Delta m$, and can be described in three ways (Fig. 10). The
589 10% valley definition applies to two adjacent peaks of equal height, which are considered
590 resolvable if the valley between them is no more than 10% of their height. In this definition, the
591 smallest resolvable mass difference is determined by the widths of the ion beam and the collector
592 slit. The second definition is quantified by the width of a single ion peak at a given fraction (e.g.,
593 50%, 5%, or 0.5%) of its maximum peak height. The 5% peak width definition is equivalent to the
594 10% valley definition. The third definition is based on the peak edge resolving power, which
595 measures how well the ion beam is defined at the source slit. This is calculated from the mass
596 difference at 5% and 95% of the maximum height on the leading edge of the peak, and it may
597 exceed the peak width resolution and the 10% valley resolution. A steeper peak corresponds to a
598 narrower beam and a higher resolving power.

599 **3.5.1.2 Mass dispersion**

600 The mass dispersion (D) of a magnetic sector mass spectrometer refers to the physical distance
601 between adjacent masses. This property is determined by its geometric configuration. For two
602 peaks at masses m and $(m + \Delta m)$, the physical distance between the two (X) is related to D by the
603 following equation:

$$604 \quad \frac{D}{X} = \frac{m}{\Delta m}$$

605 For peaks at adjacent masses ($\Delta M = 1$ amu), X corresponds to the physical separation between
606 two adjacent masses, which decreases as the analyte mass increases.

607 **3.5.1.3 Abundance sensitivity**

608 Abundance sensitivity refers to the tailing of a peak at mass m into its neighboring masses at
609 $m \pm 1$. Tailing arises primarily from collisions of high-velocity ions with background gas molecules

610 along the flight path. If collisions occur before the magnet, ions affected by the collisions will have
611 a reduced kinetic energy and be deflected more in the magnetic field than those with the same m/z
612 ratios but unaffected by the collisions. The more deflected lower-energy ions may enter the
613 collector below the correct mass. Since ions most likely lose energy during collisions, this tailing
614 effect is largely absent on the high-mass side of the peak, resulting in asymmetric tailing.
615 Alternatively, if collisions occur after the magnet, a small percentage of ions will be diverted into
616 the lower and higher mass collectors with equal possibility, resulting in symmetric tailing on both
617 sides of the peak. The effect of tailing is particularly significant when a low-intensity peak is
618 adjacent to peaks of much higher intensities.

619 **3.5.2 Motion of charged particles in electric and magnetic fields**

620 The Lorentz force describes the combined effect of electric and magnetic forces exerted on a
621 charged particle and varies in proportion to its electric charge:

$$622 \quad F = q(E + v \times B)$$

623 where F stands for the force applied to the ion, q for the electric charge ($q = ze$), E for the electric
624 field, and $v \times B$ for the cross product of the ion's velocity and the magnetic flux density.

625 The force accelerates an ion inversely proportional to its mass, according to Newton's second
626 law:

$$627 \quad F = ma$$

628 where m stands for the mass of the ion and a for the acceleration.

629 Therefore, ions in a mass spectrometer are separated by their m/z ratios. The electric force
630 accelerates an ion in the direction of the applied electric field, and a radial electric field deflects
631 incoming ions according to their velocity and kinetic energy. The magnetic force does not change

632 the speed and kinetic energy of a moving ion but deflects it along a circular path in the plane of v
633 $\times B$ according to its momentum and charge.

634 3.5.2.1 Acceleration between parallel plates

635 In the magnetic sector ICP-MS, ions are accelerated to reach a high velocity and kinetic energy
636 before entering the magnet, such that their mass separation in the magnetic field is less affected by
637 their initial kinetic energy spread, and sensitivity is improved. Assuming that an ion starts to
638 accelerate from rest and move along the electric field across a potential difference of U
639 (acceleration voltage), the change in potential energy is converted into its kinetic energy:

$$640 \quad qU = \frac{1}{2}mv^2$$

641 This acceleration gives the ion a velocity of:

$$642 \quad v = \sqrt{\frac{2qU}{m}}$$

643 At an acceleration voltage of 6-10 kV, as commonly used in MC-ICP-MS, a proton with a
644 mass of 1.67×10^{-27} kg and a charge of 1.6×10^{-19} coulombs will reach a velocity of ~1000 to
645 1400 km/s after the acceleration.

646 3.5.2.2 Deflection between cylindrical capacitors

647 An electric field between two cylindrical plates exerts a radial force that pulls ions toward its
648 center. The voltage is set such that the electric force equals the centripetal force to steer a moving
649 ion along the curve of the electrode plates with a radius of r_E :

$$650 \quad qE = \frac{mv^2}{r_E}$$

651 The radius of ion paths is determined by the kinetic energies (E_K) of ions and the potential field
652 (E) between the plates:

$$653 \quad r_E = \frac{mv^2}{qE} = \frac{2 \times \left(\frac{1}{2}mv^2\right)}{qE} = \frac{2E_K}{qE}$$

654 Ion beams with the same kinetic energy will be brought to a focus despite their divergent
655 velocity vectors at entry, achieving energy focusing (Fig. 11). In contrast, ions with slightly
656 different kinetic energies will be deflected to various degrees. By placing a narrow collimating slit
657 at either end of the electric sector, only ions that fall within the selected kinetic energy range will
658 pass through.

659 3.5.2.3 Deflection in a static magnetic field

660 A magnetic sector focuses ions with equal momentum and deflects ions with different m/z
661 ratios. When incoming ions enter a magnetic field with velocities perpendicular to the plane of v
662 $\times B$, they will be forced onto circular paths (Fig. 12A), and the magnetic force equals the centripetal
663 force:

$$664 \quad F_B = qvB = \frac{mv^2}{r_B}$$

665 The radius of the circular path r_B is given by:

$$666 \quad r_B = \frac{mv}{qB} = \frac{\sqrt{2mE_K}}{qB}$$

667 According to the equation above, singly charged ions with equal momentum will travel in
668 circles with the same radius (r). If they enter the magnetic field from a common point with a
669 divergence in the direction of α , their circular paths will intersect after traveling approximately a
670 semicircle (Fig. 12B). With small-angle approximation, a monoenergetic ion beam with an angular
671 divergence of 2α will converge to a limited width of b at the exit slit:

672
$$b \approx 2r(1 - \cos\alpha) \approx r\alpha^2$$

673 Furthermore, ions with identical kinetic energy will be deflected according to their masses,
674 whereby ions with smaller masses will be deflected more than those with higher masses. The
675 physical dispersion (D) of two masses, m and (m+Δm), along the focal plane is twice the difference
676 in the radii (Δr_B) of their circular paths through the 180° magnet (Fig. 12C). Given that

677
$$r_B = \sqrt{\frac{2U_{\square}}{qB^2}} \sqrt{m}$$

678 thus

679
$$\Delta r_B = r_B \frac{\Delta m}{2m}$$

680 and

681
$$D = 2\Delta r_B = \frac{\Delta m}{m} r_B$$

682 The natural mass dispersion of a given magnetic sector thus depends on its effective radius.

683 The equation for r_B can be rearranged as below:

684
$$\frac{m}{z} = \frac{B^2 r_B^2 e}{2U_{\square}}$$

685 This equation demonstrates that for singly charged ions, the radius of ion trajectory is
686 positively correlated with mass under a constant magnetic field and acceleration voltage. In single-
687 collector ICP-MS, ions with different masses can be sequentially focused onto the detector by
688 adjusting the magnetic field strength, the acceleration voltage, or a combination of both. This
689 allows for a complete scan of m/z ratios from low mass to high mass. However, magnet scanning
690 is slower than acceleration voltage scanning as a settling period of ~10-200 ms is required for each
691 scan to ensure a stable magnetic field. In comparison, MC-ICP-MS analyses are typically

692 performed in static mode, with both the acceleration voltage and the magnetic flux density held
693 constant, while ions with different masses are collected along a focal plane for simultaneous
694 detection.

695 **3.5.2.4 Deflection in perpendicular electric and magnetic fields**

696 If an ion enters crossed electric (E) and magnetic (B) fields with the velocity v perpendicular
697 to the lines of force of both fields, the ion will be deflected unless the electric and magnetic forces
698 are of equal magnitude but opposite directions:

$$699 \quad qE = qvB$$

700 which gives the velocity of $v = E/B$ for undeflected ions (Fig. 13). Wien (1898) used a similar
701 device to measure the m/z ratios of electrons and protons. This design led to the development of
702 the "Wien filter" as a velocity selector in ICP-MS applications (e.g., Tsuno and Ioanoviciu 2013).

703 **3.5.3 Magnetic sector mass spectrometer**

704 The magnetic sector mass analyzer has its roots in the archetypal mass spectrograph developed
705 by Thomson (1913), which led to the discovery of stable isotopes. In Thomson's experiment,
706 gaseous atoms were ionized by an electric current in a partially evacuated tube. The positively
707 charged ions were set in a circular motion by the magnetic force, while the electric field applied
708 an acceleration in the direction parallel to the magnetic field. These combined fields caused the
709 ions to leave parabolic traces on the photographic plates corresponding to their m/z ratios. The
710 resolving power of this parabola apparatus was limited to ~ 15 . As an alternative to photographic
711 film, Thomson (1912) also used a Faraday cup and an electroscope to quantify the charge intensity
712 of the beam, with which he obtained a mass spectrum. By gradually changing the magnetic field
713 strength, beams of different masses could be admitted sequentially through a slit into the Faraday
714 cup, working as a scanning mass spectrometer.

715 In separate but complementary efforts to improve the mass resolution, A. J. Dempster and F.
716 W. Aston attempted to focus ions of a certain m/z ratio onto a single detection point. Dempster
717 (1918) utilized electron bombardment to produce roughly monoenergetic ions and a 180° magnetic
718 sector to achieve direction focusing of the ions. Ions of similar kinetic energy followed
719 semicircular paths of equal radius and crossed their paths at the detector slit regardless of their
720 divergent angles at the entrance (Fig. 12B). The ions were collected in Faraday cups and detected
721 with an electrometer. This mass spectrometer provided a resolution of 100 and was particularly
722 useful for determining the relative abundances of ionic species. Bainbridge (1932) further
723 improved the resolution of the Dempster-type instrument to 500 by adding a velocity selector
724 ("Wien filter") before the magnet. Based on the mass of ${}^7\text{Li}$ measured with this instrument
725 (Bainbridge 1933), together with the masses of ${}^4\text{He}$ and ${}^1\text{H}$ reported by Aston (1927), Bainbridge
726 (1933) presented experimental proof of Einstein's mass-energy relation through the reaction of ${}^7\text{Li}$
727 $+ {}^1\text{H} \rightarrow 2{}^4\text{He}$. Dempster (1935) later introduced spark ionization to analyze conductive solids, with
728 which he discovered the rare isotope ${}^{235}\text{U}$.

729 Alternatively, Aston (1919) designed a spectrograph that compensated for ion energy spread
730 by velocity focusing, using spatially separated electric and magnetic fields. A vertical diaphragm
731 was positioned behind the electric field to select ion beams with nearly parallel velocities. Upon
732 entering the magnetic field, the ions were deflected in a direction opposite to their deflections in
733 the electric field, and ions with lower velocities were deflected more than those with higher
734 velocities in both fields. Consequently, ions with the same m/z ratio but slightly different velocities
735 arrived at the same position on the photographic plate. With this mass spectrograph, isotope masses
736 can be measured with an accuracy of 0.1% and a mass resolving power of 130. Aston (1927; 1937)
737 upgraded his first spectrograph by using finer slits, more stable and stronger electric and magnetic

738 fields that doubled ion deflection angles. These improvements increased the resolution to 2000
739 and the accuracy to $\sim 0.001\%$, which enabled Aston (1927; 1937) to precisely determine the
740 deviation of isotope masses from the whole number rule. The concept of using velocity focusing
741 together with direction focusing led to the development of double-focusing mass spectrometers, in
742 which the achievable mass resolution is not compromised by the initial divergence and energy
743 spread of ions.

744 Effective double-focusing relies on the coincidence of direction focusing with energy focusing,
745 which has benefited from the comprehensive formulation of ion trajectories through various
746 combinations of magnetic and electric fields in superimposition, or in tandem (e.g., Bartky and
747 Dempster 1929; Mattauch and Herzog 1934; Johnson and Nier 1953). The most common
748 configurations are derivatives of the Mattauch-Herzog and Nier-Johnson geometries. The
749 Mattauch-Herzog geometry uses a 31.82° electric sector followed by a 90° magnetic sector in the
750 opposite direction of curvature (Fig. 14A), offering simultaneous detection of a broad mass
751 spectrum along a focal plane. In comparison, the Nier-Johnson geometry uses a 90° electric sector
752 and a 60° magnetic sector with the same direction of curvature (Fig. 14B), which is widely used
753 in MC-ICP-MS for precise measurement of isotope ratios. In reversed Nier-Johnson geometry, the
754 magnetic sector is placed before the electric sector. This geometry is often used in single-collector
755 ICP-MS, where most ions are removed from the beam by mass filtering in the magnetic sector,
756 thereby reducing beam aberration, peak tailing, and backgrounds.

757 Sector-field mass analyzers provide flat-topped peaks and superior mass resolution (~ 300 to
758 over 10,000) for resolving isobaric interferences from analyte ions. This resolution is a significant
759 improvement over quadrupole-based instruments (~ 300 -400) that typically have the unit mass
760 resolution, as discussed in the following section. In addition, the magnetic sector provides spatial

761 separation of ions according to their m/z ratios, which facilitates the simultaneous detection of
762 multiple ion beams with a detector array, thereby minimizing the temporal fluctuations associated
763 with ionization and ion transmission for isotopic ratio analyses with MC-ICP-MS.

764 **3.5.4 Quadrupole mass spectrometer**

765 Quadrupole-ICP-MS has dominated the first decade of ICP-MS development since its
766 commercialization in 1983. It remains the most widely used ICP-MS instrument today, owing to
767 its relatively small size, mechanical simplicity, and affordable cost. A quadrupole mass filter
768 contains four cylindrical or hyperbolic rods arranged parallel in a square array (Fig. 15). The metal
769 rods are commonly 15-25 cm long, and the ion source and detector are closely packed. The mass-
770 filtering mechanism is based on applying direct and alternating electric currents to the conductive
771 rods to allow the transmission of ions of one m/z ratio at a time. A reasonably good mass resolution
772 can be achieved at a rapid scanning rate (typically 2500-5000 amu/s) and a relatively low vacuum
773 requirement ($\sim 5 \times 10^{-5}$ Torr), with no need for an additional device for energy focusing.

774 An important analytical strength of the quadrupole mass analyzer is its ease of use in tandem
775 mass spectrometry (see review by Balcaen et al., 2015). For example, both gas chromatography
776 (GC) and liquid chromatography (LC) can be conveniently interfaced with a quadrupole to identify
777 separated compounds (e.g., Finnigan 1994). Quadrupole ICP-MS is also frequently combined with
778 LA and MC-ICP-MS for in situ geochemical analyses of mineral grains. For instance, a volume of
779 laser-ablated zircon fragments can be split into a quadrupole-ICP-MS for trace elemental analyses
780 and a MC-ICP-MS for U-Pb zircon dating and Hf isotopic analyses (e.g., Yuan et al., 2008).

781 The concept of a quadrupole mass filter, published by Paul and Steinwedel (1953), differs in
782 principle from mass spectrometers that produce a spectrum of ions separated in space (magnetic
783 sector instruments) or time (time-of-flight instruments). Instead, it works analogously to an

784 adjustable bandpass filter. It utilizes oscillating electric quadrupole fields to selectively transmit
785 ions within a specific m/z range (typically \leq one mass unit) through the quadrupole each time. Ions
786 with m/z ratios beyond this narrow range will strike the rods before reaching the exit of the
787 quadrupole. The separation of ions with a specific m/z ratio is achieved by adjusting the electric
788 field and oscillating frequencies applied to the metal rods, and ions of each m/z ratio pass through
789 the quadrupole in sequence. While different masses are filtered sequentially, rapid ramping of the
790 voltages allows scanning over 0-250 amu within 100 ms. This high scanning speed gives
791 quadrupole mass spectrometers the ability to measure multiple elements rapidly.

792 The four rods of a quadrupole are arranged as two pairs in diagonal directions of the sample
793 path (Fig. 15). Both electrode pairs are supplied with a combination of constant direct current (dc)
794 of the same magnitude but opposite polarity, and RF alternating current (ac) that is 180° out of
795 phase. When no dc is applied, the RF-only electrodes serve as an ion-focusing component to direct
796 a wide range of m/z ions traveling down the quadrupole along its central axis. The ac voltages
797 applied to the electrodes focus and defocus the ion beams alternately every half period according
798 to their RF. When the rods are electrically positive, they exert equal forces on the positively
799 charged ions in opposite directions so that the ion beams converge to the center of the quadrupole
800 and get focused. By contrast, when the rods are electrically negative, the positively charged ions
801 are attracted toward the rods and defocused from the center.

802 Mass separation occurs when offsetting the ac voltage of each pair of electrodes by a constant
803 dc voltage in opposite directions to the same degree (Fig. 15). One pair of electrodes carries an
804 oscillating voltage with brief excursions to negative voltage during each period. The positively
805 charged ions are focused to the center of the quadrupole, except for a brief attraction toward the
806 rods when switched to the negative voltage. High-mass ions carry more momentum and stay longer

807 along the central axis of the quadrupole than ions with lower masses, which are attracted further
808 toward the rods when the voltages are switched to negative. These low-mass ions get increasingly
809 defocused from the central ion beam during every negative excursion of the voltages supplied to
810 the rods. Eventually, they collide with the rods and become neutralized. Therefore, this electrode
811 pair serves as a high-mass filter that blocks the transmission of ions with m/z ratios below a specific
812 value.

813 The other pair of electrodes is supplied with an oscillating voltage with brief excursions to
814 positive voltage during each period. In this case, positively charged ions are defocused from the
815 central ion beam most of the time due to attraction to the negative electrodes, except for a brief
816 focusing when the electrodes switch to positive voltage. These short excursions to positive voltage
817 within each period would only exert sufficient focusing on relatively light ions to prevent them
818 from striking the electrodes. In contrast, the brief focusing would be insufficient for ions with m/z
819 ratios above a specific value. As a result, these high-mass ions are increasingly attracted toward
820 the negative electrodes and eliminated from the ion beams as they reach the electrodes.
821 Consequently, this pair of electrodes acts as a low-mass filter. The two pairs of electrodes work
822 together to remove the transmission of ions with masses below and above a specific range at each
823 setting. This way, the voltages can be adjusted to have a narrow bandpass that allows transmission
824 through the quadrupole (Fig. 15).

825 **3.5.4.1 Mathematical expression**

826 In a quadrupole mass filter field, there is no acceleration along the central z -axis, and ions
827 travel with constant velocity along this axis. The motions along the x and y directions of the
828 symmetric hyperbolic electric field are governed by the Mathieu equation below [see Miller and
829 Denton (1986) for the derivation of these equations].

830
$$\frac{d^2u}{d\xi^2} + [a_u - 2q_u \cos(2\xi)]u = 0$$

831 where u represents the coordinate axes x or y , and

832
$$a_x = -a_y = \frac{8zeU}{mr_0^2\omega^2}$$

833
$$q_x = -q_y = \frac{4zeV}{mr_0^2\omega^2}$$

834
$$\xi = \omega t/2$$

835 where U is the magnitude of the dc voltage, $V\cos(\omega t)$ describes the amplitude of the RF voltage,
 836 ω is the angular frequency, t is time in seconds, and r_0 represents the inscribed radius between the
 837 electrodes.

838 **3.5.4.2 The a - q stability diagram**

839 The parameters a and q in the Mathieu equation correlate positively with the magnitude of the
 840 dc potential (U) and the ac potential (V) applied to a quadrupole during a scan. Solutions of the
 841 equation can be plotted in a - q space to indicate whether an ion of a given mass has a stable
 842 trajectory through the quadrupole filter at the applied voltages. Any combination of a and q that
 843 lies within the triangular area corresponds to a stable ion trajectory along the X-Z and Y-Z planes
 844 (Fig. 16A). In practice, the dc and ac potentials are adjusted proportionally so that their ratios and
 845 the resolution are held constant, forming a scan line with a slope of $2U/V$. A mass scan is
 846 completed by increasing U and V to allow ions with higher m/z ratios to pass through the
 847 quadrupole in succession (Fig. 16A and B).

848 The resolution of a quadrupole mass filter corresponds to the width of the scanning bandpass,
 849 which varies with the RF frequency and the U/V ratio. Increasing the RF frequency at a constant

850 U/V ratio causes ions to pass through more RF cycles in the quadrupole, leading to more efficient
851 separation and higher resolution. Increasing the U/V ratio leads to a steeper slope and higher mass
852 resolution, whereas decreasing the U/V ratio results in a broader bandpass (Fig. 16C) and possible
853 peak overlap between ions with similar m/z ratios. Because the stability boundary on the high-
854 mass side is steeper than that on the low-mass side, a decrease in resolution will cause the leading
855 edge of the peak to shift more toward the lower mass than the shift of the trailing edge to the higher
856 mass. Tailing on the low mass side of an ion peak can be reduced by limiting the kinetic energy
857 spread of ions entering the quadrupole.

858 The application of quadrupole mass spectrometry is mainly limited by its unit mass resolution,
859 which is insufficient to separate analyte ions from isobaric interferences in most cases. Therefore,
860 quadrupole ICP-MS is primarily used for measuring elemental concentrations at high sample
861 throughput (e.g., Houk et al., 1980; Date and Gray 1981; Date and Hutchison 1986). Stable isotope
862 analyses by quadrupole instruments are restricted to low-mass elements where natural isotope
863 fractionation is large and isobaric interferences are less of an issue. For example, Liu and Li (2019)
864 achieved a long-term precision of 1.1‰ (2SD) for Li isotope analysis using only 2.5 ng Li. They
865 pointed out that quadrupole ICP-MS is a practical alternative to MC-ICP-MS for analyzing low-
866 Li samples with high matrix contents because the quadrupole mass filter is less sensitive to matrix
867 effects, and electron multiplier detectors provide better counting statistics than Faraday cups at
868 low-Li concentrations.

869 As an advantage of its robust unit mass resolution, the quadrupole mass filter can handle
870 incoming ions with wide momentum and kinetic energy distribution. Furthermore, a quadrupole
871 is an ideal preliminary mass filter because it filters mass by varying electric fields and rapid mass
872 scanning. These analytical benefits have found wide applications in triple-quadrupole ICP-MS for

873 analyzing chemical structures or specific chemical reactions, where the first quadrupole selects a
874 specific ion to be fragmented in the second quadrupole and analyzed in the third quadrupole (e.g.,
875 Yost and Enke 1979; Yost 2022). More recently, the quadrupole has also been used as a pre-
876 collision-cell mass filter in MC-ICP-MS (e.g., Thermo-Fisher Proteus, Bevan et al., 2021; Lewis
877 et al., 2022; Mahan et al., 2022).

878 **3.5.5 Time-of-flight mass spectrometer**

879 Time-of-flight (TOF) mass spectrometers measure the mass-dependent time required for
880 microsecond pulses of accelerated ions to drift through a field-free vacuum flight tube (30-100 cm
881 long) (Fig. 17). It can generate consecutive mass spectra of ions formed by laser ablation,
882 electrothermal vaporization, and flow injection. In principle, TOF analysis is analogous to an ion
883 race (Stephens 1946; Wolff and Stephens 1953): an electric field first accelerates a package of ions
884 to the same kinetic energy. This acceleration gives each ion a characteristic velocity dependent on
885 its m/z ratio, at which it drifts along a vacuum tube. Ions with different m/z ratios are spatially
886 separated along the flight tube, and ions with lower mass reach the detector earlier than the heavier
887 ions:

$$888 \quad t = \frac{L}{v} = \sqrt{\frac{m}{z}} \times \frac{L}{\sqrt{2eV}}$$

889 The entire mass spectrum of the introduced ions is completed as ions arrive sequentially at the end
890 of the flight tube and are registered digitally. The detection of ions with various m/z ratios is quasi-
891 simultaneous as the process occurs rapidly.

892 The TOF analysis requires a precisely defined starting time for the ion race. Ions are sampled
893 in pulses instead of being introduced continuously into the flight tube, so that a lighter ion
894 introduced later would not overtake a heavier ion introduced earlier during free drift. The matrix-
895 assisted laser desorption/ionization technique (MALDI) is typically used for pulsed ionization.

896 Alternatively, ions can be released from the source in packages through electrical "gates." In cases
897 where ICP is used as the ionization source, the continuously formed ions are regulated by
898 orthogonal acceleration using a set of pulsed-repeller plates aligned horizontally to the flight tube.
899 The repeller plates send ions into the flight tube by applying a positive voltage to accelerate them
900 perpendicular to their original direction. In contrast, no ions will be admitted into the flight tube
901 when the repeller plates are uncharged. Current TOF analyzers can process up to 30,000 ion
902 packages per second; therefore, they are ideal for monitoring transient signals.

903 The major limiting factor for the mass resolution of early TOF-MS instruments is the kinetic
904 energy spread of ions prior to their admission to the flight tube (Cameron and Eggers Jr. 1948;
905 Wiley and McLaren 1955). To overcome this limitation, an electrostatic reflector, known as the
906 ion mirror, was developed (Mamyrin et al., 1973). The reflector is placed at the end of the flight
907 tube and consists of a series of high-voltage electrode rings. The reflector first decelerates the
908 incoming ions to a stop and then accelerates them again in the opposite direction (Fig. 17). In this
909 way, the initial distribution of kinetic energy between ions is compensated for by the different
910 distances the ions travel in the reflector: ions with higher velocities travel further into the reflector
911 and fly longer distances than those with lower velocities. Consequently, ions with the same m/z
912 ratio arrive at the detector concurrently regardless of their differences in kinetic energy.

913 **3.6 Detectors**

914 The detection system collects ions emerging from the mass analyzer and, based on the rate of
915 ions delivered to the detector, generates electrical signals proportional to the concentration of
916 analyte ions in a sample. The ion intensities of different m/z ratios are compared with the
917 calibration or reference standards with known concentrations. Thus, the elemental concentrations
918 in an unknown sample can be calculated. In isotopic ratio analyses, the relative beam intensities

919 of isotopes measured in a sample are compared with those of a standard. The precision of isotope
920 analyses is primarily limited by the counting statistics and the electrical Johnson-Nyquist noise of
921 the resistor in the feedback loop. This electrical noise arises from the random thermal motion of
922 electrons in an amplifier when no current is applied (Nyquist 1928).

923 Most ICP-MS analyses involve measurements of ion beam intensities ranging from sub-
924 femtoampere ($1 \text{ fA} = 10^{-15} \text{ A} = 6242 \text{ ions/s}$) to nanoampere ($1 \text{ nA} = 10^{-9} \text{ A}$), which are amplified
925 for quantification. Ion signals are typically detected by counting the number of electron pulses
926 from single ion impacts per second, or by converting the induced electric current to a voltage for
927 analog measurements (Fig. 18). Depending on the dynamic range required for the measurements,
928 ion multipliers are used to measure low ion currents (e.g., between 10^{-19} A and 10^{-13} A), whereas
929 Faraday cups are preferable for higher ion beams (e.g., between 10^{-15} A and 10^{-9} A) due to their
930 exceptional linearity and stability at high ion currents (Fig. 19). The difference in dynamic range
931 between these two types of detectors reflects their different mechanisms for detecting ions, which
932 are described below.

933 **3.6.1 Ion multipliers**

934 The number of incoming ions is "multiplied" due to the emission of secondary electrons when
935 the incident ion impacts the dynode surface of the detector. In a Daly detector (Daly 1960), positive
936 ions are attracted to an off-axis conversion dynode held at a high negative voltage ($\sim 20 \text{ kV}$), which
937 repels and accelerates secondary electrons toward a scintillator. The photons emitted from the
938 phosphor screen are amplified and detected by a photomultiplier, which can be outside the vacuum
939 chamber. In contrast, electron multipliers work under vacuum. The incident ion strikes the detector
940 surface in the line of sight, releasing secondary electrons that cascade, leading to a gain of 10^3 to

941 10^8 so that the signal is readily detected as individual electron pulses ($< 10^6$ cps) or as an electron
942 current ($\sim 10^6$ cps to $>10^9$ cps).

943 There are two main types of electron multipliers, depending on the number of electrodes used
944 (Fig. 18). In the discrete dynode multiplier, electron multiplication takes place between individual
945 dynodes that are connected by a series of resistors. The gain is adjusted by changing the negative
946 voltage (a few kV) applied to the first dynode. The voltage steps between dynodes are adjusted to
947 output the signal at ground potential. In comparison, the continuous dynode multiplier amplifies
948 the number of secondary electrons within a curved, cone-shaped glass tube. The inside of the tube
949 is coated with a thin layer of semiconducting material that has a high resistance to create a gradual
950 voltage drop along the path. A conversion dynode with a high negative voltage can be added before
951 the conventional electron multiplier so that the secondary electrons strike the multiplier with
952 substantially higher kinetic energy, thereby reducing the mass dependence of the secondary
953 electron emission.

954 Daly detectors and electron multipliers offer complementary advantages. Daly detectors are
955 more robust and deliver better linearity, especially at high count rates. Furthermore, the dynamic
956 range of Daly detectors are wider than that of electron multipliers. On the other hand, electron
957 multipliers are smaller and less expensive. They are the standard detector for single-collector ICP-
958 MS and their high signal-to-noise ratio is suitable for counting low-intensity ion beams. The
959 background noise of an ion multiplier is typically a few counts per minute, which is negligible
960 compared to ion signals of hundreds to millions per second (Carlson 2014). However, the counting
961 capability of the electron multiplier becomes limited at count rates higher than a few million cps
962 (Fig. 19), as there will be a short "dead time" (a few ns to tens of ns) during which the detector
963 cannot identify an incoming signal. Due to the restricted dynamic range of electron multipliers, a

964 Faraday cup can be added to the single-collector ICP-MS to extend the maximum countable rate
965 from 10^9 cps to 10^{12} cps, enabling measurements of trace and major elements during a single scan
966 (Wiedenbeck et al., 2012).

967 **3.6.2 Faraday cup**

968 A Faraday cup is an electrode connected to the electrical ground via a high-resistance amplifier
969 for signal integration. The Faraday cup detects ions by neutralizing their positive charges with
970 electrons flowing from the electrical ground. As the electric current passes through the amplifier,
971 it is converted to a voltage for measurement. Assuming that 10^8 ions with a fundamental electron
972 charge of 1.6×10^{-19} coulomb strike the collector per second, together they deliver a beam current
973 of 1.6×10^{-11} A, which corresponds to an output voltage of 1.6 V for a standard Faraday cup with
974 a $10^{11} \Omega$ amplifier. The use of such a high-ohm resistor for signal amplification causes a
975 background noise on the order of 10^{-16} A, which is significant compared to typical ion signals of
976 10^{-14} to 10^{-10} A (Carlson 2014), and is compensated for by an extended measurement duration of
977 several hundred seconds. Isotope abundance ratios are often measured with inter-calibrated
978 Faraday cups, as their high signal stability facilitates high-precision ratio measurements.

979 A critical consideration in designing Faraday cups is to reduce the generation and scattering
980 loss of secondary electrons. Therefore, Faraday cups have a long and narrow "bucket" shape, with
981 a base typically made of highly porous carbon. The electron trapping efficiency of the Faraday cup
982 can be enhanced by steering electrons through a magnetic field in a spiral trajectory and increasing
983 their chance of hitting the collector wall. In addition, Faraday cups have a metal slit, behind which
984 a second electrode, known as the suppressor, is inserted and supplied with a potential of -50 V to
985 -100 V (Fig. 18). This negative electrode effectively repels the secondary electrons emitted from

986 the slit when ions strike on it. It also helps to prevent the loss of electrons formed within the
987 Faraday cup by repelling them back to the base.

988 **3.6.3 Multi-detection arrangement**

989 A major advance in the ion detection system came with the coupling of a multi-collection array
990 (Fig. 18) to the ICP-MS, which enables simultaneous detection of all relevant ion signals for high-
991 precision isotopic ratio analyses (e.g., Walder and Freedman 1992; Walder et al., 1993; Wieser
992 and Schwieters 2005). Given their compact size, more than 10 Faraday cups can be readily fitted
993 into a multi-collection block, and several ion multipliers can be accommodated in addition to
994 them. Since the introduction of MC-ICP-MS, the detection system has undergone several
995 significant upgrades, including an increased number of detectors (up to 16 Faraday cups), a larger
996 dynamic range for standard Faraday cups (55 V vs. 11 V on $10^{11} \Omega$ resistors), an improved signal-
997 to-noise ratio of the Faraday cup with new amplifier designs, and a dual-mode detector
998 arrangement for convenient switching between the Faraday cup and electron multiplier.

999 The state-of-the-art multi-detection system features a switchable amplifier design to
1000 accommodate diverse applications. Amplifiers with $10^9 \Omega$ and $10^{10} \Omega$ feedback resistors facilitate
1001 the measurement of elements with isotopes that occur in significantly different abundances, such
1002 as V (e.g., Nielsen et al., 2011; Wu et al., 2016). On the other hand, amplifiers with $10^{12} \Omega$ and
1003 $10^{13} \Omega$ resistors have been developed to bridge the detection limits between Faraday cups and ion
1004 multipliers (Fig. 19) (e.g., Wieser and Schwieters 2005; Breton et al., 2015). Results from
1005 Koornneef et al. (2014) show that with a 100-fold increase in resistivity, the signal-to-noise ratio
1006 of the amplifier is improved by a factor of up to five. Furthermore, the $10^{13} \Omega$ Faraday cup
1007 potentially offers higher precision than electron multipliers for beam sizes greater than 20 kcps.
1008 This new amplifier has greatly expanded the potential for high-precision isotopic analyses for

1009 small-sized samples (e.g., laser ablation, carbonate, or biological samples) and low-abundance
1010 isotopes (e.g., Ta and Re) using MC-ICP-MS (Pfeifer et al., 2017; Steinmann et al., 2019; e.g.,
1011 Dellinger et al., 2020; Grigoryan et al., 2020).

1012

1013 **4 Analytical interferences in ICP-MS**

1014 While a highly efficient ICP source offers valuable analytical benefits, the trade-off is that a
1015 variety of interfering species could be introduced into the analyzer region along with the ions of
1016 interest. These interferences are the main factor limiting the accuracy and precision of ICP-MS
1017 analyses. They can be divided into two broad groups, i.e., spectral and non-spectral, which are
1018 discussed below.

1019 **4.1 Spectral interferences**

1020 Spectral interferences occur when unwanted ionic species, either isobaric or polyatomic, have
1021 the same nominal m/z ratio as the analyte ions. These interferences result in spectral overlap,
1022 causing the true analyte signal to be overestimated. Isotopic analysis is particularly susceptible to
1023 spectral interferences as it requires the measurement of two or more interference-free isotopes. In
1024 contrast, a small amount (0.1-1%) of spectral overlap can be tolerated in elemental analysis.
1025 Spectral interferences originate from various sources, including the sample matrix, solvent (e.g.,
1026 H_2O , HNO_3 , and HCl), plasma gas (typically Ar), and plasma-entrained air (e.g., N_2 , O_2 , and CO_2).
1027 Isobaric interferences occur when other elements have naturally occurring isotopes at the same
1028 mass as the analyte (e.g., Ar, K, and Ca at mass 40). Polyatomic interferences arise from the
1029 combination of two or more atomic ions, typically in the form of Ar-related species, oxide and
1030 hydroxide, and Cl-, S-, or P-based species.

1031 When Ar serves as the plasma gas, the most common interferences are Ar^+ , Ar_2^+ , and argides.
1032 Argon has three naturally occurring isotopes: ^{36}Ar (0.337%), ^{38}Ar (0.063%), and ^{40}Ar (99.6%).
1033 ^{40}Ar is a severe isobaric interference on ^{40}K , a minor isotope of K (0.0117%). It also interferes
1034 with ^{40}Ca (94.961%), the dominant Ca isotope. The various combinations of Ar isotopes form a
1035 series of interferences on Se isotopes, particularly $^{40}\text{Ar}_2$ that interferes with the major Se isotope
1036 (^{80}Se). A variety of Ar-related polyatomic ions can form in the mass range between 14 and 90 due
1037 to the combination of Ar with the sample solvent (e.g., Tan and Horlick 1986). For example,
1038 $^{40}\text{Ar}^{16}\text{O}^+$ interferes with the dominant Fe isotope ($^{56}\text{Fe}^+$), while $^{40}\text{Ar}^{14}\text{N}^+$ and $^{40}\text{Ar}^{16}\text{O}^1\text{H}^+$ interfere
1039 with $^{54}\text{Fe}^+$ and $^{57}\text{Fe}^+$, respectively. Argides also significantly affect K isotope measurements, with
1040 $^{38}\text{ArH}^+$ and $^{40}\text{ArH}^+$ directly interfering with $^{39}\text{K}^+$ and $^{41}\text{K}^+$, respectively. For samples containing
1041 organics, $^{40}\text{Ar}^{12}\text{C}$ may interfere with the dominant Cr isotope (^{52}Cr), and $^{40}\text{Ar}^{14}\text{N}$ may interfere
1042 with ^{54}Cr .

1043 While an ICP source produces mainly singly charged ions, a small percentage of other ionic
1044 forms may be present. Doubly charged ions occur mostly in alkaline earth elements, forming
1045 interference peaks at half their masses (e.g., $^{48}\text{Ca}^{2+}$ on $^{24}\text{Mg}^+$). Refractory elements typically
1046 combine with ^1H , ^{16}O , or $^{16}\text{O}^1\text{H}$ from the air or sample solvent to form molecular interferences
1047 such as hydrides, oxides, and hydroxides. For example, Ti has five naturally occurring isotopes:
1048 ^{46}Ti (7.99%), ^{47}Ti (7.32%), ^{48}Ti (73.98%), ^{49}Ti (5.46%), and ^{50}Ti (5.25%). Their oxides form
1049 interferences on ^{62}Ni ($^{46}\text{Ti}^{16}\text{O}$), ^{63}Cu ($^{47}\text{Ti}^{16}\text{O}$), ^{64}Zn ($^{48}\text{Ti}^{16}\text{O}$), ^{65}Cu ($^{49}\text{Ti}^{16}\text{O}$), and ^{66}Zn ($^{50}\text{Ti}^{16}\text{O}$).
1050 The formation of oxides relative to atomic ions depends on their respective bond strength with
1051 oxygen, and is particularly problematic for refractory elements with high bond strength (e.g.,
1052 REEs, Ba, and Ca).

1053 **4.2 Non-spectral interferences**

1054 In contrast to spectral interferences that directly overlap with the m/z ratio of the analyte, non-
1055 spectral interferences reflect changes in analyte throughput between samples due to physical and
1056 chemical differences in the sample matrices. The physical properties of the sample matrices, such
1057 as viscosity, surface tension, evaporation rate, and vapor pressure, can affect the ionization
1058 temperature in the plasma or the mass discrimination as an ion beam passes through the expansion
1059 chamber (Longerich 1989). In addition, analyte transmission efficiency is susceptible to matrix
1060 elements. For example, a high loading of easily ionizable elements (e.g., Na) to the plasma may
1061 reduce plasma energy and suppress the ionization of analytes. The suppression of the analyte signal
1062 can also be due to space charge effects in the interface region, where coulomb repulsion between
1063 positively charged ions defocuses the ion beams (Gillson et al., 1988; Tanner 1992). If a sample
1064 contains an excess of heavy matrix elements, the lighter analyte ions will be more strongly
1065 deflected from the central ion path than the heavier matrix ions, resulting in a lowered analyte
1066 sensitivity.

1067

1068 **5 Approaches to overcome interferences**

1069 Spectral and non-spectral interferences significantly affect the accuracy of elemental
1070 concentration and isotopic ratio analyses; therefore, they must be eliminated or corrected
1071 appropriately. An ideal approach to avoid spectral interferences of an analyte is to measure the
1072 signals of its interference-free isotopes with relatively high natural abundances. However, this
1073 approach does not apply to elements with isotopes of low natural abundances, or with only a single
1074 isotope (e.g., As, Co, Sc, and Mn). Therefore, various alternative approaches have been developed
1075 to reduce the interferences with ICP-MS (e.g., see reviews by Evans and Giglio 1993; Lum and

1076 Leung 2016). It is important to emphasize that the most practical approaches should be tailored for
1077 the specific element.

1078 **5.1 Choice of sample solvents**

1079 For ICP-MS measurements, samples are usually dissolved in dilute HNO₃ because its three
1080 constituent elements are also present in the entrained atmospheric gases. In contrast, HCl is less
1081 frequently used because Cl readily forms complex ions interfering with analyte ions. This is
1082 particularly the case for As, which occurs only as ⁷⁵As (overlapping with ⁴⁰Ar³⁵Cl⁺), and for V,
1083 which has its dominant isotope (⁵¹V) overlapping with ³⁵Cl¹⁶O⁺. Sulfuric acid and H₃PO₄ are
1084 generally not recommended because they can form a variety of S- and P-bearing polyatomic ions.
1085 For example, ³²S¹⁶O⁺ and ³¹P¹⁶O¹H⁺ are direct interferences on ⁴⁸Ti⁺, and ³²S¹⁶O₂⁺ is a direct
1086 interference on ⁶⁴Zn⁺. In addition, ³¹P¹⁴N⁺ interferes with ⁴⁵Sc, the only Sc isotope, and ³¹P¹⁶O₂⁺
1087 interferes with ⁶³Cu, the major Cu isotope. One effective approach to suppress hydride formation
1088 is to replace H₂O with D₂O, which eliminates the major polyatomic interference of ³⁶ArH⁺ on
1089 ³⁷Cl⁺, thereby enabling the accurate determination of ³⁷Cl/³⁵Cl ratios (Smith and Houk 1990).

1090 **5.2 Analyte-matrix separation**

1091 For precise and accurate isotopic analyses, it is recommended to separate the analyte from the
1092 matrix elements. Chromatographic separation is commonly used, and is based on affinity to the
1093 ion exchanger, hydrophobic/hydrophilic properties, size (size-exclusion chromatography), or other
1094 less frequently used methods. Chromatographic separation can be performed online or offline,
1095 depending on the nature of the sample and analyte. Matrix components that readily form insoluble
1096 compounds can be removed by precipitation. For example, Cl-related interferences can be
1097 removed by adding AgNO₃ to precipitate as AgCl (Lyon et al., 1988). Precipitation of Ca in the
1098 form of calcium sulfates has also been used to separate Mg from Ca in carbonates (Bao et al.,

1099 2019). Alternatively, a vapor generation device can be used to convert hydride-forming elements
1100 into volatile species, which are subsequently separated and concentrated from the residual
1101 solutions (e.g., Powell et al., 1986; Buckley et al., 1992; and see section 3.1.3).

1102 **5.3 Sample desolvation**

1103 Because water is the primary source of H- and O-related polyatomic interferences, the
1104 formation of these molecular ions can be effectively reduced by a desolvation nebulization system
1105 (e.g., Gustavsson and Hietala 1990; and see section 3.1.2.2). This method applies to all elements,
1106 regardless of their tendency to form volatile species. As measured by the ratios of CeO^+/Ce^+ , oxide
1107 formation decreases from 3.5% for typical "wet" plasma introduction to 0.01-0.08% for various
1108 designs of "dry" plasma introduction systems, with an increase in sensitivity by at least an order
1109 of magnitude.

1110 **5.4 Modifying the plasma**

1111 **5.4.1 Mixed-gas plasma**

1112 By feeding an extra gas to a desolvation nebulization system, it is possible to further reduce
1113 polyatomic interferences, mass bias, and oxide formation (e.g, Lam and McLaren 1990). This
1114 additional gas is usually blended into the nebulizer gas, as this causes less plasma perturbation and
1115 is more efficient than mixing it into the coolant gas at a much higher flow rate. The most commonly
1116 used gas is N_2 , a molecular gas with a similar ionization energy to Ar (Fig. 1(a)) but a higher
1117 thermal conductivity and electrical capacity. The presence of N changes the electrical and spectral
1118 properties of the Ar plasma, its ionic composition, and the population of Ar energy levels.

1119 The principal ionization mechanism in an Ar- N_2 plasma may differ from that in an all-Ar
1120 plasma. It has been suggested that abundant metastable Ar atoms are present in Ar plasma, which
1121 can be readily ionized to Ar^+ , or they can enhance the ionization of analyte elements by Penning

1122 ionization (Boumans and De Boer 1977). In an Ar-N₂ plasma, the energy of the lower metastable
1123 level of Ar atoms is slightly higher than the excitation of vibrational levels of N₂ molecules by
1124 electron impact. This leads to efficient collisional energy transfer that quenches the metastable Ar
1125 by exciting the vibrational levels of N₂ molecules (Wagatsuma and Hirokawa 1989). The reduced
1126 density of metastable Ar in the plasma makes Penning ionization of the analyte less likely. On the
1127 other hand, the N₂, N₂⁺, and N⁺ species are highly active in scavenging O₂ to form NO⁺. Based on
1128 ion distributions measured in a mixed Ar-N₂ plasma, ionization is suggested to occur primarily by
1129 charge transfer with NO⁺, N₂⁺, or Ar⁺ (Houk et al., 1983; Holliday and Beauchemin 2002; Holliday
1130 and Beauchemin 2003).

1131 The formation of polyatomic and oxide interferences can be significantly reduced in an Ar-N₂
1132 plasma where ionization is dominated by charge transfer with NO⁺. Adding low-flow of N₂ (30
1133 mL/min, < 5% vol./vol.) to the nebulizer gas has been shown to considerably reduce the formation
1134 of ArCl⁺, ArAr⁺, and ArO⁺, possibly due to the competitive formation of N-based polyatomic
1135 species (Evans and Ebdon 1989; Evans and Ebdon 1990). In addition, the ionization energy of
1136 NO⁺ is lower than that for most Ar- and Cl-based polyatomic interferences, which limits their
1137 production in an Ar-N₂ plasma. The formation of NO⁺ also effectively sequesters oxygen, thereby
1138 reducing oxide production (Lam and Horlick 1990; Holliday and Beauchemin 2003). Moreover,
1139 N actively quenches excited state pathways of certain oxide species in the expansion chamber, as
1140 illustrated by NdO⁺ (Newman et al., 2009). Finally, the presence of N in the nebulizer gas has also
1141 been shown to mitigate the effects of matrix elements on sensitivity (van der Velde-Koerts and de
1142 Boer 1994).

1143 Along with the reduced formation of polyatomic ions in a mixed Ar-N₂ plasma, it has been
1144 observed that the sensitivity of many elements increases with careful optimization of gas flow

1145 rates, sampling depths, and other parameters. The addition of N₂ causes the plasma volume to
1146 contract along the torch axis (Greenfield and McGeachin 1978; Choot and Horlic 1986; Lam and
1147 Horlick 1990; Sesi et al., 1994), thus the power density increases around its toroidal region. Since
1148 N₂ has a higher thermal conductivity than Ar, the presence of N₂ may lead to enhanced energy
1149 transfer from the toroidal region of the plasma to its central channel. However, N₂ molecules also
1150 absorb energy, which results in the cooling of the central channel. Therefore, the amount of N₂
1151 added to the nebulizer gas likely affects the competition between energy loss to the central channel
1152 and energy transfer from the toroidal region. In ICP-OES and ICP-MS analyses, signal
1153 enhancement is generally observed at a low flow rate of N₂. In contrast, high flow rates of N₂ can
1154 lead to signal reduction or even plasma extinction (see review by Scheffler and Pozebon 2014).

1155 The effect of N₂ addition on signal enhancement depends on the element being analyzed,
1156 particularly its ionization energy and its tendency to form a strong metal-oxygen bond. The
1157 efficient formation of NO⁺ molecules in an Ar-N₂ plasma would reduce oxygen availability for
1158 metals that tend to form oxides, and these metals may exhibit a corresponding increase in ionic
1159 signals (Lam and Horlick 1990). In addition, charge transfer with NO⁺ can enhance the ionization
1160 of elements with relatively high ionization energies. The improved thermal conductivity in Ar-N₂
1161 plasma may also be responsible for the observed signal enhancements, as supported by a broad
1162 positive correlation between the signal enhancement factor and ionization energy of various
1163 elements in LA-ICP-MS measurements (Hu et al., 2008).

1164 **5.4.2 Cold plasma**

1165 Operating the Ar plasma at a reduced RF power (i.e., cold plasma) can effectively suppress the
1166 formation of Ar-related spectral interferences (Jiang et al., 1988). This method leverages the high
1167 ionization energy of Ar compared to elements with masses similar to Ar and its polyatomic ions

1168 (e.g., K, Ca, Fe, Cr, and Cu, see Fig. 1). Elements with sufficiently low ionization energies can be
1169 efficiently ionized in a cold plasma while the ionization of Ar is strongly reduced. Moreover,
1170 ionization in a cold plasma is suggested to occur primarily via charge transfer with NO^+ , similar
1171 to that in a mixed Ar- N_2 plasma (Tanner 1995; Holliday and Beauchemin 2002). Therefore, when
1172 using cold plasma, especially with a desolvation nebulization system, NO^+ becomes the
1173 predominant background species, while Ar^+ , ArO^+ , and ArH^+ are significantly reduced (Jiang et
1174 al., 1988).

1175 The use of cold plasma has shown enhanced detection limits for elemental concentrations (low
1176 ppt levels) and improved precision for isotope ratio measurements, as studied for Li, Fe, K, and
1177 Ca (e.g., Sakata and Kawabata 1994; Tanner et al., 1995; Murphy et al., 2002). Notably,
1178 Chernonozhkin et al. (2017) have shown that a precision of $\pm 0.04\%$ (2SD) can be achieved for
1179 $^{56}\text{Fe}/^{54}\text{Fe}$ ratios with a low mass resolving power ($\text{RP}_{\text{edge } 5,95\%}$) of 300, owing to negligible
1180 interferences from $^{40}\text{Ar}^{16}\text{O}^+$ (on $^{56}\text{Fe}^+$) and $^{40}\text{Ar}^{14}\text{N}^+$ (on $^{54}\text{Fe}^+$) and reduced instrumental mass
1181 discrimination using cold plasma (600 W) (Fig. 20). This level of precision is similar to that
1182 typically achieved using hot plasma (1260 W), with which a significantly higher $\text{RP}_{\text{edge } 5,95\%}$ of
1183 4500 is required to resolve Ar-related interferences. Likewise, direct measurement of the $^{44}\text{Ca}/^{40}\text{Ca}$
1184 ratio with MC-ICP-MS is made possible by a decreased $^{40}\text{Ar}/^{40}\text{Ca}$ ratio from 0.1 to 0.002 when
1185 the RF power is reduced from 1250 W to 400 W (Fietzke et al., 2004). In addition to Ar, carbon-
1186 based interferences (C_2^+ , C_2H^+ , C_2H_2^+ and CN^+) are significantly reduced, which facilitates high-
1187 precision measurements of Mg isotopes (Choi et al., 2012) and Li isotopes (Bryant et al., 2003;
1188 Choi et al., 2013), particularly for the analysis of low-Li carbonate samples using single-collector
1189 quadrupole ICP-MS (Misra and Froelich 2009).

1190 While cold plasma is a valuable option for analyzing elements susceptible to Ar-related
1191 interferences, it has several potential drawbacks compared with conventional hot plasma (Tanner
1192 1995; Bryant et al., 2003). First, non-spectral interferences appear to be greater under cold plasma
1193 conditions. Second, oxide formation may be more pronounced for some metals under cold plasma
1194 conditions. For example, the formation of $^{40}\text{CaO}^+$ would directly interfere with $^{56}\text{Fe}^+$ and
1195 underestimate the $^{40}\text{Ca}^+$ signal. Third, certain interferences remain at significant levels, and in these
1196 cases, a combination of cold plasma and high mass resolution is necessary, such as for the accurate
1197 determination of $^{41}\text{K}^+$ ($^{40}\text{Ar}^1\text{H}^+$), $^{57}\text{Fe}^+$ ($^{40}\text{Ar}^{16}\text{O}^1\text{H}^+$), and $^{54}\text{Fe}^+$ ($^{40}\text{Ar}^{14}\text{N}^+$). Considering these
1198 limitations, hot plasma is preferred for most elements due to its higher sensitivity and stability.

1199 **5.5 Collision/reaction cell**

1200 Collision/reaction cell (CRC) technology has found diverse applications before being adapted
1201 for removing polyatomic interferences in ICP-MS. The early development of CRC was motivated
1202 by research in the physical chemistry of gaseous ions. For example, Von Zahn and Tatarczyk
1203 (1964) used an RF-only quadrupole field in a pressurized flight tube between two mass
1204 spectrometers to quantify collision-induced dissociations (CID) of polyatomic ions. Futrell and
1205 Miller (1966) added a collision chamber between two double-focusing mass spectrometers to study
1206 ion-molecule reactions. In subsequent studies, the sector-field mass spectrometers were replaced
1207 by two quadrupole mass filters to improve the ion transmission efficiency (Iden et al., 1972; Yu et
1208 al., 1972), and an RF-only quadrupole was inserted in between for photodissociation of polyatomic
1209 ions (Vestal and Futrell 1974; McGilvery and Morrison 1978). In a following study, Yost and Enke
1210 (1978) introduced triple quadrupole mass spectrometry to analytical chemistry, with mass
1211 selection of ions in the first quadrupole, collisional fragmentation of selected ions in the second
1212 quadrupole (RF-only), and analysis of fragmented ions in the third quadrupole. Since then, this

1213 configuration has become widely adopted for structural and trace mixture analyses of complex
1214 organic molecules (Yost and Enke 1979; Yost 2022).

1215 Several techniques have been explored to remove polyatomic interferences using CID. Initial
1216 experiments with triple quadrupole mass spectrometers yielded promising results from glow
1217 discharge mass spectra, suggesting that specific polyatomic ions (e.g., ArO^+) can be eliminated or
1218 reduced by dissociating their chemical bonds (King and Harrison 1989). However, using ICP-MS,
1219 Douglas (1989) found that the collision energy required to dissociate many polyatomic ions is
1220 greater than the difference in ionization energy between the analyte ions and the Ar atoms. As a
1221 result, CID would promote the neutralization of analyte ions by electrons transferred from Ar
1222 atoms. In this case, the loss of analyte ions due to scattering and charge transfer outweighs the
1223 benefit of dissociating polyatomic ions by collision. Nevertheless, D.J. Douglas noticed that Ce^+
1224 reacted with O_2 much more efficiently than CeO^+ when air was introduced into the quadrupole and
1225 suggested that ion-molecule chemistry in a collision cell might help alleviate molecular
1226 interferences.

1227 Rowan and Houk (1989) investigated the potential for chemical resolution of polyatomic
1228 interferences using a quadrupole collision cell connected between the ICP source and a quadrupole
1229 mass filter. They observed effective attenuation of Ar_2^+ , ArO^+ , and ArN^+ when Xe or CH_4 were
1230 used for the reactions, and efficient removal of unwanted ions by kinetic energy discrimination.
1231 Subsequent work has elaborated on the high selectivity of ion-molecule chemistry using different
1232 gases (H_2 , O_2 , and CH_4) to remove plasma matrix ions (Barinaga et al., 1994; Koppelaar et al.,
1233 1994; Eiden et al., 1996; Eiden et al., 1997; Eiden et al., 1999). At the same time, efforts were
1234 made to reduce the substantial loss of analyte ions (30-50%) due to collisions with the background
1235 gas. Douglas and French (1992) reported improved ion transmission by feeding the cell with a

1236 buffer gas, which provides collisional focusing of the ion beam. Further improvements in
1237 transmission were achieved by using a higher-order multipole (Eiden et al., 1997; Turner et al.,
1238 1997; Feldmann et al., 1999). These improvements led to commercially available CRC-equipped
1239 ICP-MS instruments.

1240 The use of RF-driven multipole CRC in ICP-MS has been discussed in detail by Koppenaal et
1241 al. (2004). The choice between quadrupole, hexapole, or octopole depends on the specific
1242 analytical purpose. A quadrupole offers the unique advantage of selecting target ions through a
1243 narrow, user-chosen m/z range while rejecting all ions outside this range. However, a quadrupole
1244 produces a steep and narrow potential field (Fig. 21) that requires collisional focusing to reduce
1245 scattering losses. It is thus necessary to use relatively heavy molecular gases with large cross-
1246 sections (e.g., NH_3 and CH_4) to induce abundant ion-molecule interactions. In comparison, lighter
1247 gases (e.g., He and H_2) are generally used in a hexapole or octopole because they have wider and
1248 flatter potential well minima, which result in a larger ion stability region that allows simultaneous
1249 transmission of ions with different masses at high efficiency (Fig. 21). Furthermore, the larger ion
1250 stability region in higher-order multipoles ensures a greater gas thickness (at comparable
1251 pressures), which increases the number of collisions and, thus, the reaction efficiency. In summary,
1252 a quadrupole CRC works with more reactive gases, while a hexapole or octopole CRC works with
1253 more selective gases.

1254 In essence, CRC is a type of ion-guiding lens pressurized with gases. When filled with a
1255 chemically inert gas (e.g., He), it acts as a collision cell that attenuates polyatomic interferences
1256 by kinetic energy discrimination (Fig. 22). Because polyatomic ions have larger sizes than atomic
1257 analytes with the same nominal mass, they would collide more frequently with the buffer gas and
1258 lose more kinetic energy. These low-energy polyatomic interferences can thus be readily filtered

1259 out at the exit of the cell by applying a bias voltage. However, kinetic energy discrimination is less
1260 effective for isobaric interferences that occur as singly and doubly charged ions (Fig. 23A), which
1261 require chemical resolution (Fig. 23B-D).

1262 When the CRC is supplied with a reactive gas (e.g., H₂), ion-molecule reactions are the primary
1263 mechanism to achieve chemical resolution between analyte ions and spectral interferences (see
1264 reviews by Tanner et al., 2002; Balcaen et al., 2015). By supplying a specific reactive gas, ion-
1265 molecule chemistry can either occur exclusively with the spectral interferences to eliminate them
1266 from the m/z region of interest (on-mass reaction mode, Fig. 23B), or the reaction gas selectively
1267 reacts with the atomic ions of interest to form molecular ions that can be measured in a higher m/z,
1268 'cleaner' region (mass-shift mode, e.g., detection of ⁷⁵As⁺ as ⁷⁵As¹⁶O⁺). In mass-shift mode, it is
1269 possible that certain matrix elements in the sample (e.g., ⁹¹Zr⁺) form isobaric interferences with
1270 the product molecular ions (⁷⁵As¹⁶O⁺, Fig. 23C). A mass filter can be added before the reaction
1271 cell to reject non-target masses (Fig. 23D), ensuring that the ions entering the reaction cell are not
1272 affected by the composition of the sample matrices.

1273 The on-mass reaction mode is widely used in ICP-MS to electrically neutralize and remove
1274 Ar-related interferences (e.g., Ar⁺, ArO⁺, ArCl⁺, and ArH⁺). This process involves charge transfer
1275 between the interference species and the reaction gas, taking advantage of the high ionization
1276 energy of Ar-based interferences (≥ 15.76 eV) compared to most analyte ions. Spontaneous charge
1277 transfer occurs when the ionization energy of the reaction gas is lower than that of the interfering
1278 species but higher than that of the analyte ions (Fig. 24A). Hydrogen gas with an ionization energy
1279 of 15.42 eV is often used to react with Ar⁺, while the analyte ions are unaffected. The reaction
1280 forms simple product ions with low m/z ratios (Eiden et al., 1996). For example, electrons can be

1281 spontaneously transferred from H₂ to Ar⁺ (e.g., Ar⁺ + H₂ → Ar + H₂⁺), freeing m/z = 40 for the
1282 measurement of ⁴⁰Ca⁺.

1283 On-mass interferences can also be eliminated by converting into a new ionic species with a
1284 different m/z ratio. These reactions typically involve proton transfer (AH⁺ + B → BH⁺ +A),
1285 hydrogen atom transfer (A⁺ + BH → AH⁺ +B), and hydride ion transfer (A⁺ + BH → B⁺ +AH)
1286 due to the fast reaction rate of small-sized hydrogen (Tanner et al., 2002). For instance, ArO⁺ and
1287 ArOH⁺ have lower ionization energies than H₂, so they cannot be neutralized by charge transfer
1288 with H₂. Instead, these interferences can be removed through successive exothermic reactions of
1289 ArO⁺ + H₂ → ArOH⁺ + H and ArOH⁺ + H₂ → H₂O⁺ + Ar + H (Arnold et al., 2008). Another
1290 example is the proton transfer reaction of ArH⁺ + H₂ → H₃⁺ +Ar to remove ArH⁺, which is a major
1291 interference on ⁴¹K⁺ (e.g., Li et al., 2016).

1292 Instead of using a gas to selectively react with the interferences (i.e., the on-mass reaction
1293 mode), the mass-shift mode increases the mass of an analyte ion by a known value, thus separating
1294 it from the spectral interferences. This approach is particularly useful for ionic species that exhibit
1295 significantly different chemical reactivity toward a specific reactive gas. Oxidation is commonly
1296 used because it exploits the large difference in oxygen affinity between the atomic ions of interest
1297 and the polyatomic interferences (Fig. 24(b)). General oxidizing agents such as N₂O and CO₂ have
1298 the advantage of forming stable reaction products (e.g., N₂ and CO). In comparison, targeted
1299 oxidation of specific ions can be achieved by reactions with O₂ or NO, which require strong A⁺-O
1300 bonding. Exothermic oxidation by O₂ has facilitated the measurement of S and P concentrations
1301 by converting them to SO⁺ and PO⁺, thereby shifting their masses away from those of polyatomic
1302 interferences (e.g., NO⁺, NOH⁺, CH₃O⁺, ¹⁶O₂⁺) (Bandura et al., 2002).

1303 The mass-shift mode has also been applied to in situ Rb-Sr dating with LA-ICP-MS(-MS)
1304 (e.g., Moens et al., 2001; Cheng et al., 2008). These applications are based on the significantly
1305 different electronic configurations of $\text{Sr}^+(\text{s}^1)$ and $\text{Rb}^+(\text{s}^0)$, which result in their distinctive chemical
1306 reactivities. $\text{Sr}^+(\text{s}^1)$ is highly reactive toward a variety of gases (denoted as MX) and forms Sr-
1307 bearing complexes, such as SrF^+ by F-atom transfer with CH_3F and SF_6 , SrCl^+ by Cl-atom transfer
1308 with CH_3Cl , and SrO^+ by O-atom transfer with N_2O . In contrast, $\text{Rb}^+(\text{s}^0)$ has a noble-gas electronic
1309 configuration and is inert or reacts only very sluggishly with these gases. Therefore, the ratios of
1310 $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ can be measured as $^{87}\text{SrMX}/^{86}\text{SrMX}$ and $^{87}\text{Rb}/^{86}\text{SrMX}$, respectively.

1311 The CRC has proven to be an effective and affordable technique for overcoming spectral
1312 interferences in quantitative elemental analysis with the ICP quadrupole mass spectrometer. Its
1313 previous application in magnetic sector mass spectrometers was limited to a discontinued single-
1314 focusing MC-ICP-MS (i.e., IsoProbe-P, Feldmann et al., 1999). This instrument primarily utilized
1315 the CRC to reduce the ion kinetic energy spread (from 20-30 eV to ≤ 2 eV) by collisional energy
1316 damping; therefore, high-precision isotopic analysis can be performed (Turner et al., 1997).
1317 IsoProbe-P has achieved variable levels of success in determining isotope ratios, particularly for
1318 isotopes that are severely affected by polyatomic interferences but are of significant planetary,
1319 geological, and biological importance, such as Si (Chakrabarti and Jacobsen 2010; Sun et al.,
1320 2010), Fe (Guilbaud et al., 2010), Se (Rouxel et al., 2002), Ca (Huang et al., 2010), and K (Li et
1321 al., 2016; Wang and Jacobsen 2016). These promising results have sparked interest in using a CRC
1322 on double-focusing MC-ICP-MS for more precise and accurate isotopic analysis.

1323 Currently, four models of MC-ICP-MS offer a CRC option, all of which utilize an RF-only
1324 hexapole. The Sapphire model, manufactured by Nu Instruments, features a switchable
1325 conventional mode and CRC mode (Fig. 25). The conventional mode functions as a Nu Plasma 3

1326 double-focusing MC-ICP-MS with an acceleration voltage of 6 kV. When switching to the CRC
1327 mode, ions are first accelerated with a voltage of 4 kV and then slowed down slightly before
1328 entering an off-axis CRC. After the reaction, the ion beam is focused onto the exit slit and
1329 reaccelerated by a voltage of 4 kV. Compared with isotopic analyses performed using high mass
1330 resolution with considerably reduced sensitivity (e.g., Hu et al., 2018; Morgan et al., 2018), the
1331 Sapphire CRC mode provides high-precision isotopic analyses for K (Ku and Jacobsen 2020; Chen
1332 et al., 2021; Moynier et al., 2021; Li et al., 2022; Zheng et al., 2022; An et al., 2023), Ca (Dai et
1333 al., 2022; Gao et al., 2022), and Fe (Wang et al., 2022) using low mass resolution without
1334 compromising the sensitivity. The CRC unit can also be implemented on the Nu Sapphire 1700
1335 platform with an extended geometry (An et al., 2023), achieving high chemical resolution and high
1336 mass resolution.

1337 The other three models of CRC-MC-ICP-MS are built on platforms from Thermo Fisher
1338 Scientific, with the addition of a pre-cell mass filter to select the m/z "windows" entering the CRC
1339 (Fig. 26). This configuration is promising for laser-ablation applications that do not require
1340 chemical purification of the analyte. A prototype model named Proteus was built by combining
1341 the ion source, a modified quadrupole mass filter, and the CRC of the iCAP-Q-MS with a Neptune
1342 Plus MC-ICP-MS. While this instrument has been used for high-precision K (Mahan et al., 2022)
1343 and Ca (Lewis et al., 2022) isotopic analyses and in situ Rb-Sr dating (Bevan et al., 2021), its
1344 analytical capability was limited by the low sensitivity and strong non-exponential mass bias
1345 associated with the quadrupole mass filter (Craig et al., 2021). To overcome these limitations, an
1346 upgraded prototype instrument named Vienna was developed. This instrument, commercially
1347 known as Neoma, features a double "Wien filter" for mass selection and is tailored for coupling
1348 with the Neptune XT MC-ICP-MS (Craig et al., 2021). The potential of this new instrument has

1349 been successfully demonstrated by a study of in situ ^{87}Rb - ^{87}Sr measurements on minerals using
1350 SF_6 gas (Dauphas et al., 2022) and high-precision Cu isotopic analysis using helium gas to remove
1351 $^{40}\text{Ar}^{23}\text{Na}^+$ interferences on $^{63}\text{Cu}^+$ (Télouk et al., 2023). The conventional applications of Neoma
1352 were also illustrated by high-precision K (Télouk et al., 2022), U (Zirakparvar et al., 2023), and Ti
1353 (Deng et al., 2023) isotopic analyses.

1354 **5.6 High-resolution**

1355 For ICP-MS instruments with a magnetic sector, their inherent high mass resolution can
1356 physically separate spectral interferences from analyte masses (e.g., Bradshaw et al., 1989). This
1357 method is a convenient alternative to chemical resolution with a CRC. It has been widely used for
1358 precise and accurate isotopic analysis where two or more isotopes need to be measured without
1359 the influence of interfering species. Typically, three options for mass resolving power ($\text{RP}_{\text{edge } 5,95\%}$)
1360 are achievable, ranging from low (~ 300 - 400) through medium (~ 4000 - 9000) to high (≥ 10000).
1361 The state-of-the-art MC-ICP-MS instruments are capable of providing an $\text{RP}_{\text{edge } 5,95\%} \geq 15000$,
1362 either by an innovative slit design (for Nu Plasma HR, II, 3, and Nu Sapphire) or by the use of an
1363 additional ultra-high-resolution (XHR) unit (for Neptune XT and Neoma MC-ICP-MS). These
1364 high-resolution instruments are well suited for the isotopic analyses of Si, Mg, Cl, and K (e.g.,
1365 Hobin et al., 2021).

1366 The mass resolution of an instrument can be adjusted by varying the slit widths. The Nu
1367 Instruments MC-ICP-MS, for example, has three types of slits: the source slit with three width
1368 options (0.03, 0.05, and 0.3 mm, Fig. 27A), the two symmetrical alpha slits that can be adjusted
1369 continuously from 0-7 mm (Fig. 27B), and three sets of collector slits (0-1 mm) located in front of
1370 the low, medium, and high mass collectors (Fig. 27C). For high-precision analysis, the collector
1371 slit is usually wider than the ion beam, i.e., the source image (Fig. 27D). During the mass scan, the

1372 entire ion beam is collected and appears as a flat-topped peak, so that slight or transient shifts in
1373 the ion image position in the focal plane have a negligible effect on the measured intensity and
1374 precision. In contrast, if the beam is as wide as the collector slit, any mass instability would have
1375 a significant effect on the registered signal.

1376 In low-resolution mode, all slits are set to their maximum widths. Polyatomic ions may overlap
1377 with the peaks of the analytes in the absence of a CRC (Fig. 28A and B). Narrowing the source
1378 slit and the collector slit leads to a steeper peak slope and a higher mass resolution (Fig. 27D and
1379 28C-E). The two alpha slits reduce the aberration of a diverging beam by passing a small current
1380 through each alpha slit wire, which cuts off the beam from both sides until the beam intensity is
1381 halved (Fig. 27(b)). The adjustable collector slit can then be moved to improve the alignment of
1382 the analyte peaks and their separation from the interferences (Fig. 27C). As a trade-off for the
1383 increased resolution, the sensitivity is reduced by a factor of ~10 in medium resolution and 15-20
1384 in high resolution.

1385 In most applications, polyatomic interferences occur on the high-mass side of the analyte peaks
1386 (Fig. 28C). Isotopic measurements can be performed on the low-mass side, where an interference-
1387 free, flat-topped section is provided by setting the collector coincidence to block the interfering
1388 ions (Fig. 28D). This pseudo-high-resolution mode is preferred over the true high-resolution mode
1389 (Fig. 28E) because it provides a wider flat-topped peak shoulder for the analysis. However,
1390 interferences can occur on both sides of the analyte ions, especially if the analyte elements have
1391 not been chemically separated from the matrix elements prior to isotopic analysis (e.g., in laser
1392 ablation applications). For example, $^{48}\text{Ca}^{2+}$ occurs on the low-mass side of the Mg isotope peaks,
1393 while $^{12}\text{C}^{14}\text{N}^+$, $^{12}\text{C}_2^{1}\text{H}_2^+$, $^{12}\text{C}^{13}\text{C}^+$, and $^{12}\text{C}_2^+$ occur on the high-mass side. In this case, the true high-

1394 resolution mode is necessary as it allows complete separation of the interferences from the analyte
1395 peaks without further reducing the beam sensitivity (Fig. 28E and F).

1396 To achieve high resolution with improved ion transmission, Nu Instruments introduced a large-
1397 geometry double-focusing MC-ICP-MS, i.e., the Nu Plasma 1700, in 1999. It features a
1398 substantially wider mass dispersion of ~ 1700 mm compared to conventional MC-ICP-MS (~ 500
1399 mm), achieved by combining a 943 mm radius, 70° sector electrostatic analyzer with a 750 mm
1400 radius, 70° laminated magnet. The large geometry offers a high base resolution of > 800 (10%
1401 valley definition), which is sufficient for analyzing approximately 40% of the isotopes at 100%
1402 ion transmission. The flat-topped peak, which is critical for isotopic ratio analysis, can be
1403 maintained at a 10% valley resolution of > 5000 (e.g., Fig. 28F). Additional features of this
1404 instrument include a continuously adjustable source entrance slit and independent collector slits
1405 that allow variable resolutions to be set for individual collectors. These features lead to a wide
1406 range of selectable $RP_{\text{edge } 5,95\%}$ from 5000 to 30000. For a given resolving power, the Nu Plasma
1407 1700 has considerably higher transmission than a conventional MC-ICP-MS. A major limitation
1408 of this instrument is being unable to resolve $^{36}\text{Ar}^+$, $^{40}\text{Ar}^+$, and Ar_2^+ from $^{36}\text{S}^+$, $^{40}\text{Ca}^+$ and $^{80}\text{Se}^+$,
1409 respectively. This limitation motivated the invention of the *Nu* Sapphire 1700 CRC-MC-ICP-MS.

1410

1411 **6 Instrumental isotope fractionation**

1412 An inherent issue with ICP-MS analysis is mass-dependent ion transmission efficiency,
1413 resulting in preferential extraction and transmission of heavier ions through the interface and ion
1414 optic system. This instrumental mass bias poses a particular challenge for isotope ratio
1415 measurements. The magnitude of this bias varies with the analyte mass, ranging from $<1\%$ /amu
1416 for heavy elements (e.g., Hf, Tl, Pb, and U) to $\sim 20\%$ /amu for light elements such as Li and B (Fig.

1417 29). To obtain accurate isotopic ratios, it is crucial to correct the instrumental isotope fractionation
1418 appropriately. The two general correction methods for stable isotope ratio measurements are
1419 double spike and standard-sample bracketing (with or without element doping). Comprehensive
1420 reviews of different correction methods can be found in the literature (e.g., Albarède et al., 2004;
1421 Yang 2009; Albarède et al., 2015; Yang et al., 2018; Klaver and Coath 2019), and brief
1422 descriptions are provided below.

1423 **6.1 Double-spike approach**

1424 The most robust correction is the isotope mixture approach and its derivative, the double-spike
1425 method, whereby the sample solution is mixed with a double-spike solution enriched in two
1426 isotopes relative to their natural abundances (Nier 1950; Dodson 1963; Rudge et al., 2009). If the
1427 spike is added during sample digestion, the isotope fractionation generated during sample
1428 preparation, chromatographic purification, and instrumental analyses are all corrected by assuming
1429 an identical fractionation being passed onto the double-spike. In cases where the isotope ratio of
1430 an unknown sample can be related to that of the reference standard by a mass fractionation factor
1431 α :

$$1432 \quad R_{sample} = R_{standard} \cdot \left(\frac{m_j}{m_i}\right)^\alpha$$

1433 where m_i and m_j are masses of the denominator and numerator isotopes, respectively, the isotopic
1434 ratio of a spiked sample solution can be solved from the mixing equation:

$$1435 \quad R_{mixture} = \frac{R_{double-spike} \times q + R_{sample} \times C \times (1 - q)}{q + C \times (1 - q)}$$

1436 where C represents the relative isotopic abundance of the denominator isotope in the sample to
1437 that in the double-spike, and q quantifies the mole fraction of double spike in the mixture.

1438 Assuming that instrumental isotope fractionation follows the exponential law with a fractionation
1439 factor of β :

1440
$$R_{mixture} = r_{mixture} \times \left(\frac{m_j}{m_i}\right)^\beta$$

1441 the three equations are combined to the equation below:

1442
$$f(q, \alpha, \beta) = R_{double\ spike} \times q + R_{standard} \times \left(\frac{m_j}{m_i}\right)^\alpha \times C \times (1 - q) - r_{mixture} \times \left(\frac{m_j}{m_i}\right)^\beta \times [q +$$

1443
$$C \times (1 - q)] = 0$$

1444 The instrumental mass bias (β) can be solved along with the isotope fractionation of a sample
1445 relative to a reference standard (α) and the mole fraction of double spike in the mixture (q) by
1446 inverting the three mixing equations using three independent isotope ratios.

1447 The double-spike approach has the advantage of providing both high-precision isotope ratios
1448 and elemental abundances. In addition, it does not require strict 100% recovery of the target
1449 element from chromatographic separation; therefore, it is preferred for elements (especially trace
1450 elements) that are difficult to completely isolate from the sample matrix without sacrificing the
1451 chemical yields, such as Ni (e.g., Gueguen et al., 2013), Mo (e.g., Siebert et al., 2001; Anbar
1452 2004), Cr (e.g., Schoenberg et al., 2008), Zr (e.g., Inglis et al., 2018), and Ti (e.g., Millet and
1453 Dauphas 2014), or for elements susceptible to evaporative loss during sample preparation, such as
1454 Sn (e.g., Creech et al., 2017; Wang et al., 2018; She et al., 2023). Accurate and precise isotopic
1455 determination with the double-spike approach relies on a well-calibrated double-spike composition
1456 and an optimal spike proportion in the spike-sample mixture. Furthermore, it requires the analyte
1457 element to have four or more stable isotopes. An exceptional case is that with a critical double-
1458 spike composition and an optimal q , the mixing equations are insensitive to β , so that it can be
1459 estimated by analyzing a reference standard. This critical mixing double-spike approach can be

1460 applied to elements with three isotopes, such as Mg, Si, and K (Hofmann 1971; Bizzarro et al.,
1461 2011; Coath et al., 2017; He et al., 2022). Special attention must be paid to double-spike data
1462 reduction for extraterrestrial samples with isotope anomalies because they do not follow mass-
1463 dependent fractionation (Hu and Dauphas, 2017).

1464 **6.2 Standard-sample bracketing approach**

1465 Standard-sample bracketing, in which standards and samples are measured sequentially, is a
1466 generally applicable approach for correcting instrumental isotope fractionation in MC-ICP-MS
1467 analysis if the analytes are fully recovered from the column with a clean separation (e.g., Halicz
1468 et al., 1999; Tomascak et al., 1999; Belshaw et al., 2000; Galy et al., 2001). This approach takes
1469 advantage of the fast sample analyses and the relatively stable instrumental isotope fractionation
1470 in MC-ICP-MS, as sample solutions are continuously aspirated into the ionization source. The two
1471 essential assumptions for using the standard-sample bracketing correction are (1) a linear drift of
1472 the instrumental isotope fractionation over a short period and (2) an identical instrumental isotope
1473 fractionation for the sample as for the standard. Accordingly, the instrumental fractionation is
1474 corrected by normalizing the isotopic ratio of the sample to the average of the two adjacent
1475 bracketing standards. The isotopic ratio of an unknown sample is expressed as per mil (‰)
1476 deviation from the bracketing standard:

$$1477 \quad \delta_{sample} (\text{‰}) = \left(\frac{R_{sample}}{0.5R_{standard1} + 0.5R_{standard2}} - 1 \right) \times 1000$$

1478 The delta value of each bracketing standard can be calculated from the two neighboring
1479 bracketing standards in a similar way:

$$1480 \quad \delta_{standard_n} (\text{‰}) = \left(\frac{R_{standard_n}}{0.5R_{standard_{n-1}} + 0.5R_{standard_{n+1}}} - 1 \right) \times 1000$$

1481 This calculation describes instrumental stability based on the reproducibility of the delta values
1482 calculated for all bracketing standards measured during an analytical session. Since the number of
1483 measurements on bracketing standards is significantly larger than the number of repeat
1484 measurements on a given sample, the two standard deviation (2SD) of $\delta_{\text{standards}}$ provides a more
1485 conservative error estimate than that based on limited numbers of sample analyses (Dauphas et al.,
1486 2009; Teng et al., 2015).

1487 The application of standard-sample bracketing requires neither the choice of a specific law to
1488 describe instrumental mass fractionation nor *a priori* of the true isotopic ratio of the bracketing
1489 standard. Nevertheless, this method does not correct for artifacts due to the presence of matrix
1490 elements or other differences between the samples and the bracketing standards. Therefore,
1491 accurate and precise isotopic determination requires a high degree of elemental purification and
1492 matching of the analyte concentration and acid molarity between samples and bracketing standards
1493 (e.g., Hu and Teng 2019).

1494 The bracketing standard and sample solutions can be doped with an element of similar mass
1495 and a known isotopic ratio to potentially correct for the non-linear drift of instrumental mass
1496 fractionation and to mitigate matrix effects. Many studies have followed the original work of
1497 Longerich et al. (1987) and assume that elements with similar masses have a similar instrumental
1498 isotopic fractionation coefficient (β) in MC-ICP-MS. As an example, Ni-doping can be used in Fe
1499 isotope analysis, assuming that

1500
$$\beta_{Ni} = \ln \left[\frac{({}^{62}\text{Ni}/{}^{60}\text{Ni})_{\text{measured}}}{({}^{62}\text{Ni}/{}^{60}\text{Ni})_{\text{reference}}} \right] / \ln \left(\frac{M_{62Ni}}{M_{60Ni}} \right)$$

1501 then

$$\left(\frac{{}^{56}\text{Fe}}{{}^{54}\text{Fe}} \right)_{corrected} = \left(\frac{{}^{56}\text{Fe}}{{}^{54}\text{Fe}} \right)_{measured} \left(\frac{M_{56\text{Fe}}}{M_{54\text{Fe}}} \right)^{\frac{\ln[(62\text{Ni}/60\text{Ni})_{reference}/(62\text{Ni}/60\text{Ni})_{measured}]}{\ln(M_{62\text{Ni}}/M_{60\text{Ni}})}}$$

1503 The corrected ratios are used to calculate the delta values of the samples. However, Maréchal
 1504 et al. (1999) demonstrated that for Cu and Zn, β_{Cu} and β_{Zn} could differ by 10%, while their ratio
 1505 remain constant during an analytical session. Therefore, Maréchal et al. (1999) suggested
 1506 calculating the β_{Cu}/β_{Zn} ratio from the slope of the linear regression between drifts in $\ln({}^{65}\text{Cu}/{}^{63}\text{Cu})$
 1507 and $\ln({}^{68}\text{Zn}/{}^{64}\text{Zn})$ of an admixed Zn standard solution [slope = $\beta_{Cu}/\beta_{Zn} \times$
 1508 $\ln(M_{65\text{Cu}}/M_{63\text{Cu}})]/\ln(M_{68\text{Zn}}/M_{64\text{Zn}})$, and applying this relationship to calculate the Cu isotopic
 1509 difference between the sample and the standard (and vice versa for Zn isotopic analyses).

1510

1511 7 Concluding remarks and future directions

1512 Mass spectrometry has progressed to achieve accurate analysis of isotope abundances and
 1513 ratios with higher precision using smaller samples, owing to upgraded introduction systems,
 1514 interface designs, ion lenses, and vacuum and detection systems. The development of Hf and W
 1515 isotopic measurements using MC-ICP-MS has transformed the field of geochronology (e.g.,
 1516 Vervoort et al., 1996; Blichert-Toft and Albarède 1997; Albarède et al., 2000; Kleine et al., 2002;
 1517 Yin et al., 2002). The instrumental improvements have also led to the ability to resolve isotopic
 1518 variations of transition metals and heavy elements that were previously limited by analytical
 1519 uncertainties. For example, nucleosynthetic isotope anomalies have been detected in meteorites
 1520 for a growing number of elements, revealing the compositional heterogeneity across the Solar
 1521 System at various scales (e.g., Trinquier et al., 2009; Zhang et al., 2012; Dauphas 2017; Schiller
 1522 et al., 2018; Kleine et al., 2020; Kruijer et al., 2020; Schiller et al., 2020; Hopp et al., 2022; Onyett
 1523 et al., 2023). In particular, as initially suggested by Savage et al. (2014), the recent identification

1524 of nucleosynthetic isotope anomalies of moderately volatile Zn provides unequivocal evidence for
1525 the contribution of both carbonaceous and non-carbonaceous materials to Earth's volatile inventory
1526 (Paquet et al., 2022; Savage et al., 2022; Steller et al., 2022; Martins et al., 2023). The stable
1527 isotope fractionations of moderately volatile elements and refractory elements have also
1528 contributed significantly to our understanding of the sources and formation processes from
1529 chondrules to terrestrial bodies (e.g., Luck et al., 2003; Luck et al., 2005; Luais 2007; Wombacher
1530 et al., 2008; Day and Moynier 2014; Kato et al., 2015; Wang and Jacobsen 2016; Kato and Moynier
1531 2017; Pringle et al., 2017; Nie and Dauphas 2019; van Kooten and Moynier 2019; Hellmann et al.,
1532 2020; Ku and Jacobsen 2020; Hu et al., 2021; Nie et al., 2021; Tian et al., 2021; Wang et al., 2021;
1533 Hu et al., 2022; 2023; Koefoed et al., 2023; Nie et al., 2023; Paquet et al., 2023; Wang et al., 2024).

1534 Metal stable isotopic variations in terrestrial rocks have been used to trace major episodes of
1535 geologic activity throughout Earth's history, including variations in oxygen levels in the
1536 atmosphere and oceans (e.g., Pogge von Strandmann et al., 2015; Stüeken et al., 2015; Chi Fru et
1537 al., 2016; Zhang et al., 2018; Ostrander et al., 2019), the intensity of forward and reverse
1538 weathering of silicates and its influence on long-term climate cycle (e.g., Pogge von Strandmann
1539 et al., 2021; Cao et al., 2022), the linkage between extreme paleoenvironments and mass
1540 extinctions (e.g., Payne et al., 2010; Huang et al., 2016; Liu et al., 2017; Zhang et al., 2021; Shen
1541 et al., 2022), the process and timing of subduction initiation, as well as the nature and mechanism
1542 of Archean continental crust formation (e.g., André et al., 2019; Deng et al., 2019; Antonelli et al.,
1543 2021; Huang et al., 2022; Deng et al., 2023; Tian et al., 2023), the cycling of surface materials
1544 (including carbon) to the sub-arc and deep mantle (e.g., Elliott et al., 2006; Beunon et al., 2020;
1545 Banerjee et al., 2021; Huang and Jacobsen 2021; Debret et al., 2022; Liu et al., 2022; Zhang et al.,
1546 2022). There is also a growing interest in using metal stable isotopes in the fields of environmental

1547 science (e.g., Cloquet et al., 2008; Weiss et al., 2008; Yin et al., 2010; Blum et al., 2014;
1548 Wiederhold 2015; Schilling et al., 2021; Balaram et al., 2022; Basu et al., 2022; Johnson et al.,
1549 2022; Sullivan et al., 2022; Qu and Han 2023), ecology and bioarchaeology (e.g., Jaouen and Pons
1550 2017; Martin et al., 2017; Hassler et al., 2018; Stephens et al., 2021; Martin et al., 2022), and bio-
1551 medical science (e.g., von Blanckenburg et al., 2009; Balter et al., 2013; Moynier et al., 2013;
1552 Balter et al., 2015; Albarède et al., 2017; Moynier et al., 2017; Costas-Rodríguez et al., 2019;
1553 Mahan et al., 2020; Moynier et al., 2020; Tacail et al., 2020; Schilling et al., 2021; Hill Gallant
1554 and Zheng 2022; Morel et al., 2022; Schilling et al., 2022; Sullivan et al., 2023).

1555 More recently, CRC-MC-ICP-MS has shown great promise in removing Ar-related
1556 interferences, which enables the measurement of K, Ca, and Fe isotope ratios without resorting to
1557 the pseudo-high-resolution mode that leads to a substantial sensitivity loss. Another advantage of
1558 the CRC-MC-ICP-MS is that ^{40}Ca is directly measurable, with limited isobaric interference from
1559 ^{40}Ar . These improvements provide the opportunity to further investigate the Ca isotopic
1560 composition of the bulk Solar System and terrestrial bodies (e.g., Klaver et al., 2021; Eriksen and
1561 Jacobsen 2022; Fu et al., 2022; Moynier et al., 2022; Fu et al., 2023), to apply ^{40}K - ^{40}Ca dating (Dai
1562 et al., 2023), to identify the presence of short-lived ^{41}Ca as ^{41}K excess in chondritic components
1563 (Ku et al., 2022), and to explore biological applications of metal isotopes (e.g., Moynier et al.,
1564 2021; Higgins et al., 2022; Mahan et al., 2022; Télouk et al., 2022; Cui et al., 2023a; b). In addition,
1565 the mass-shift mode of CRC has been successfully applied to in situ Rb-Sr dating (Bevan et al.,
1566 2021; Dauphas et al., 2022). The potential of CRC-MC-ICP-MS is far from fully realized. With
1567 significantly improved sensitivity, the isotopic ratios of many elements can be analyzed with
1568 minimal sample consumption. Future studies could be targeted at detecting small-scale isotopic
1569 variations, such as in minerals and their inclusions, experimental products, and mission return

1570 samples (e.g., Moynier et al., 2022; Hu et al., 2024), at coupling a laser ablation system to the
1571 CRC-MC-ICP-MS (e.g., Bevan et al., 2021; Dauphas et al., 2022), or at investigating ion-
1572 chemistry with various gases and extending the CRC techniques to other isotope systems that are
1573 plagued by polyatomic interferences (e.g., Se and Si).

1574 Another direction for future exploration is the development of ICP using an alternative plasma
1575 gas to increase the ionization efficiency and to reduce polyatomic interferences. For example,
1576 many limitations of argon plasma could be overcome by using helium plasma (Abdallah and
1577 Mermet 1982; Robin et al., 1982; Chan and Montaser 1985; Chan et al., 1986; Montaser et al.,
1578 1987); because helium consists primarily of ^4He (natural abundance 99.9998%), which has an
1579 extremely low m/z ratio of 4. Furthermore, helium has a considerably higher ionization energy
1580 (24.6 eV) than argon; therefore, helium plasma is expected to enhance the ionization efficiency of
1581 elements. The analytical performance of neon plasma has also been investigated using laser
1582 ablation (LA)-ICP-MS to analyze solid materials, where Ar-related interferences are reduced
1583 (Petibon et al., 2002). It is worth noting that commercial instruments are optimized for argon
1584 plasma. Using an alternative plasma gas may require a major adjustment in the RF generator's
1585 matching circuits, forward power, torch configuration, and pumping capacity in the interface.

1586 Since W. Wien observed the deflection of positively charged particles in a magnetic field and
1587 J. J. Thomson's discovery of isotopes a century ago, mass spectrometry has evolved from a
1588 technique for studying atomic structures into an essential tool for molecular, elemental, and
1589 isotopic ratio analyses. The development of self-sustaining, atmospheric ICP with an aqueous
1590 sample introduction system has facilitated multi-element analysis with unprecedented flexibility,
1591 detection limits, and sample throughput. The coupling of ICP with a quadrupole mass analyzer has
1592 made ICP-MS a worldwide popular analytical technique. The integration of double-focusing

1593 magnetic sector MS with a multi-collector detection system (MC-ICP-MS) has further
1594 revolutionized the field, enabling accurate and precise isotopic analysis of metals and metalloids
1595 across the Periodic Table. The utilization of collision/reaction cell technology on modern MC-
1596 ICP-MS has offered a novel approach to removing spectral interferences. Future endeavors to
1597 improve interface design and reduce space charge effects will allow the potential of ICP-MS to be
1598 better exploited. The constant pursuit of higher mass resolution and analytical precision, accuracy,
1599 and sensitivity will continue to push the analytical boundaries of ICP-MS, fueling interdisciplinary
1600 research in the broad fields of cosmochemistry, geosciences, environmental sciences, and
1601 biological and medical sciences.

1602

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1613

1614 **Figure captions**

1615

1616 Fig. 1. Argon ICP as an efficient ionization source. (A) Ionization energy (eV) of elements as a
1617 function of their atomic mass. (B) Degree (%) of ionization of elements as a function of their
1618 ionization energy, adapted from the calculated results by Houk (1986) based on Saha Equation at
1619 an ionization temperature (T_{ion}) of 7500 K with an electron density (n_e) of $1 \times 10^{15}/\text{cm}^3$. Argon
1620 efficiently ionizes most elements except for non-metals, metalloids, and certain metals (e.g., Hg),
1621 which are indicated by the red circles and labels. While most elements form singly charged positive
1622 ions, alkali earth and rare earth elements may form doubly charged ions because their second
1623 ionization energies are lower than the first ionization energy of argon.

1624

1625 Fig. 2. Main components of double-focusing ICP-MS equipped with a multi-collector detection
1626 system.

1627

1628 Fig. 3. Typical types of nebulizers used for sample introduction into the ICP-MS. (A) Concentric
1629 nebulizers; (B) Crossflow nebulizers; (C) Nebulizer transport efficiency as a function of sample
1630 uptake rate. Source: (A) and (C) are reproduced with permission from Glass Expansion, and (B)
1631 is modified from Olesik (2014) with permission from Elsevier.

1632

1633 Fig. 4. Typical types of spray chambers used for condensing large droplets ($> 10 \mu\text{m}$) produced by
1634 nebulizers. (A) A baffled cyclonic spray chamber; (B) A dual Scott/cyclonic spray chamber.
1635 Reused with permission from Glass Expansion.

1636

1637 Fig. 5. Examples of commercially available desolvation systems. (A) CETAC Aridus 3 uses a
1638 heated spray chamber with a microporous membrane to remove solvent vapors. (B) Elemental
1639 Scientific Inc. (ESI) Apex combines a heated spray chamber with a cold condenser and a heated
1640 membrane desolvator to remove solvent vapors. Reused with permission from Teledyne LABS for
1641 (A) and ESI for (B).

1642

1643 Fig. 6. Sensitivity enhancement for elements between Li and U using “dry” plasma (Apex
1644 desolvating nebulizer system) and direct injection nebulization (d-DIHEN) relative to “wet”
1645 plasma using stable introduction system (SIS: dual Scott/cyclonic spray chamber). Adapted from
1646 Louvat et al. (2011) with permission from John Wiley and Sons.

1647

1648 Fig. 7. (A) Illustration of a glass ICP torch and (B) Torch box configuration.

1649

1650 Fig. 8. Interface design for ICP-MS. (A) Differential pressure levels in ICP-MS across its main
1651 components, from the ICP at atmospheric pressure to the high-vacuum mass analyzer region. A
1652 high vacuum is required for ions to have a long mean free path to travel through the mass
1653 spectrometer and reach the detector. The relationship between mean free path and pressure is

1654 plotted based on data reported on the Pfeiffer Vacuum website for nitrogen at 273.15 K. The
1655 horizontal axis of the plot is in reverse order (decreasing pressure). (B) An illustration of ion
1656 extraction from the interface region. Modified from Olesik (2014) and Campargue (1984), with
1657 permission from Elsevier and the American Chemical Society, respectively. The small gray insert
1658 shows an older interface design using a much smaller sampling orifice, which is characterized by
1659 a thicker boundary layer and electron-poor sheath. Adapted from Niu and Houk (1996) with
1660 permission from Elsevier.

1661
1662 Fig. 9. Schematic illustration of zoom lenses used on *Nu* Instruments MC-ICP-MS for adjusting
1663 the mass dispersion of isotopes of interest. (A) Quad lenses increase the dispersion for U isotopes.
1664 (B) Sr isotopes separated by the natural dispersion of the magnet. (C) Sr isotopes with the correct
1665 spacing produced by the Quad lenses. Reproduced with permission from Nu Instruments Ltd.

1666
1667 Fig. 10. Three commonly used definitions of resolution in mass spectrometry: (A) 10% valley
1668 definition; (B) peak width definition; (C) peak edge definition.

1669
1670 Fig. 11. An electrostatic analyzer brings diverging ions of identical kinetic energy into focus and
1671 disperses incoming ions according to their kinetic energies. Ions having a higher kinetic energy
1672 (E_{K2}) are deflected less relative to those with a lower kinetic energy (E_{K1}).

1673
1674 Fig. 12. Ion deflection in a static magnetic field. (A) Circular trajectory of a moving ion in a
1675 magnetic field. (B) Angular focusing of ions with identical kinetic energy in a perpendicular
1676 magnetic field (shown in light blue). (C) Mass dispersion of a 180° magnetic field at the focal
1677 plane.

1678
1679 Fig. 13. The application of crossed electric and magnetic fields as a velocity selector ("Wien filter")
1680 in the mass spectrometer.

1681
1682 Fig. 14. Simplified illustration of the two commonly used configurations for double-focusing: (A)
1683 Mattauch-Herzog geometry; (B) Forward Nier-Johnson geometry. Adapted from Jakubowski et
1684 al., (2011) with permission from the Royal Society of Chemistry.

1685
1686 Fig. 15. Schematic representation of a quadrupole mass analyzer. One pair of electrodes serve as
1687 the low-mass filter and the other pair serve as the high-mass filter. The two electrode pairs result
1688 in a narrow bandpass of approximately 1 amu. Adapted from Miller and Denton (1986) and
1689 Vanhaecke and Degryse (2012) with permission from the American Chemical Society and John
1690 Wiley and Sons, respectively.

1691
1692 Fig. 16. Illustration of Mathieu stability diagram for a quadrupole ICP-MS. At a lower U/V ratio
1693 (a shallower slope scan line), the mass resolution is reduced while ion transmission is increased.

1694 Adapted from Clases (2023) with permission from the Royal Society of Chemistry under CC-BY
1695 3.0 license.

1696
1697 Fig. 17. Schematic representation of an orthogonal-acceleration time-of-flight mass spectrometer
1698 (TOF MS) coupled to a quadrupole ICP. Adding a reflector improves the mass resolution; different
1699 travel distances in the reflector compensate for the kinetic energy distribution of ions with the same
1700 m/z ratio. Adapted from Hendriks et al. (2017) with permission from the Royal Society of
1701 Chemistry.

1702
1703 Fig. 18. Schematic illustrations of common ion detectors used in ICP-MS, with the Faraday cup
1704 on the left and ion multipliers on the right. The illustration(s) for the Faraday cup and electron
1705 multiplier are adapted from Wiedenbeck et al., (2012) with permission from John Wiley and Sons,
1706 for the Daly detector is adapted from Daly (1960) with permission from AIP Publishing, and for
1707 the multi-collector arrangement is reproduced with permission from Nu Instruments Ltd.

1708
1709 Fig. 19. Dynamic range of different detector types. The recommended detector(s) available for a
1710 given signal intensity are indicated by the intensity of shading. The counting statistic limit on
1711 precision for a 10-minute acquisition is shown at the top, with the typical limit for each detector
1712 type on the right. Provided by Thermo Fisher and reused with permission.

1713
1714 Fig. 20. An illustration of using cold plasma to effectively reduce Ar-related interferences for Fe
1715 isotopic analysis. Mass scans in (A) and (B) were performed in medium mass resolution ($m/\Delta m =$
1716 4500) using “wet” plasma introduction at different RF powers. Compared with (A) hot plasma
1717 conditions (1260 W), the interferences of $^{40}\text{Ar}^{16}\text{O}^+$ (on $^{56}\text{Fe}^+$) and $^{40}\text{Ar}^{14}\text{N}^+$ (on $^{54}\text{Fe}^+$) become
1718 negligible under (B) cold plasma conditions (600 W), allowing $^{56}\text{Fe}/^{54}\text{Fe}$ ratios to be measured
1719 precisely in low mass resolution mode ($m/\Delta m \sim 300$). However, a small amount of $^{40}\text{Ar}^{16}\text{O}^1\text{H}^+$
1720 persists, and interferes with the minor isotope of ^{57}Fe . Reproduced from Chernozhkin et al.
1721 (2017) with permission from the Royal Society of Chemistry.

1722
1723 Fig. 21. A comparison of the potential well (upper panel) and ion stability regions (blue field in
1724 the lower panel) between a quadrupole, a hexapole, and an octopole. Adapted and modified from
1725 Marchante-Gayón et al. (2003) with permission from the Royal Society of Chemistry.

1726
1727 Fig. 22. Principles of kinetic energy discrimination in a collision cell. A narrower ion energy
1728 distribution leads to a better separation between the analyte ions and the polyatomic interferences.
1729 Reproduced with permission from Thermo Fisher.

1730
1731 Fig. 23. Schematic representation of four different modes of CRC operation. (A) Collision mode:
1732 a buffer gas is added to the cell to filter out the slightly more massive polyatomic ions based on
1733 kinetic energy discrimination. (B) On-mass reaction mode: charge exchange reactions with H_2

1734 remove 40Ar^+ and ArH^+ interferences, freeing m/z of 39, 40, and 41 for K isotope measurements.
1735 (C) Conventional mass-shift mode: $^{75}\text{As}^+$ is oxidized to $^{75}\text{As}^{16}\text{O}^+$ and measured at $m/z = 91$, which
1736 overlaps with the isobaric interference of $^{91}\text{Zr}^+$. (D) Mass-shift mode with pre-cell mass filtering:
1737 the first quadrupole admits only ions at $m/z = 75$ to the cell while those with other m/z values (e.g.,
1738 $^{91}\text{Zr}^+$) are rejected. $^{75}\text{As}^+$ is then converted to $^{75}\text{As}^{16}\text{O}^+$ by O_2 and measured at $m/z = 91$. Adapted
1739 and modified from Balcaen et al. (2015) with permission from Elsevier.

1740
1741 Fig. 24. Chemical reactions to remove isobaric interferences via (A) electron transfer and (B)
1742 oxygen atom transfer with various gases. In (A), atomic ions are labeled in black color, and their
1743 oxides and chlorides are shown in blue and green color, respectively. If the first ionization energy
1744 (indicated on the y-axis) of an interfering species is higher than the reaction gas (indicated by the
1745 dashed lines), it is thermodynamically favorable to neutralize the interfering ions by electron
1746 transfer from the gas. In (B), atomic ions of analytical interest are shown as solid circles and
1747 interferences (argon, argide, oxide, and hydroxide) are shown as open circles. The horizontal
1748 dashed lines represent oxygen atom affinities of gases with one less oxygen than their indicated
1749 forms. If an ion has an oxygen-atom affinity (shown on the y-axis) above a dashed line, it is
1750 thermodynamically favorable to incorporate an oxygen atom from the corresponding gas. Ion
1751 oxides with oxygen-atom affinities lower than the dashed line readily give up an oxygen atom to
1752 the corresponding neutral, which has one less oxygen atom than the indicated gas. Adapted from
1753 Koyanagi et al. (2005) and Tanner et al., (2002), with permissions from John Wiley and Sons and
1754 Elsevier, respectively.

1755
1756 Fig 25. Schematic representation of the dual-path design of *Nu* Sapphire CRC-MC-ICP-MS. The
1757 application of the Conventional Mode, as illustrated by K isotopic analysis (Hu et al., 2018), is
1758 compared with the use of Collision/Reaction Cell (CRC) Mode to remove Ar-based interferences
1759 for K and Ca isotopic measurements. Modified from figures provided by Nu Instruments Ltd with
1760 permission.

1761
1762 Fig. 26. Schematic representations of CRC-MC-ICP-MS built on Thermo Fisher Scientific
1763 platforms with a pre-cell mass filter. (A) Proteus; (B) Vienna; (C) Neoma. Neoma is commercially
1764 available, while Proteus and Vienna are prototypes. (A) and (B) are from Craig et al. (2021) with
1765 permission from American Chemical Society under CC-BY 4.0 license, and (C) is adapted from
1766 Dauphas et al. (2022) with permission from the Royal Society of Chemistry under CC-BY 3.0
1767 license.

1768
1769 Fig. 27. Three types of slits and their respective locations on a *Nu* Instruments MC-ICP-MS for
1770 mass resolution adjustment. (A) Source slit (0.03 mm, 0.05 mm, and 0.3 mm); (B) Alpha slits (0-
1771 7 mm); (C) Collector slits (0-1 mm); (D) Registered peak shape after two spatially resolved beams
1772 (with dispersion D and width b) swept across a Faraday cup (with collector slit width W_C).
1773 Modified from figures provided by Nu Instruments Ltd with permission.

1774

1775 Fig. 28. Different mass resolution modes used in MC-ICP-MS. (A) In low-resolution mode, a
1776 collision/reaction cell provides interference-free flat-topped peaks for Fe isotopes. (B) Without a
1777 collision/reaction cell, the polyatomic interferences overlap with the Fe isotope peaks in low-
1778 resolution mode. (C) and (D) In pseudo-high-resolution mode, Fe isotope peaks are partially
1779 resolved from the polyatomic interferences, providing an interference-free peak shoulder for
1780 isotope ratio analyses. (E) and (F) In true high-resolution mode, Fe isotope peaks are fully
1781 separated from the polyatomic interferences. The large-geometry Nu Plasma 1700 provides wider
1782 flat-topped peaks than the standard MC-ICP-MS. Modified from figures provided by Nu
1783 Instruments Ltd with permission.

1784

1785 Fig. 29. Instrumental mass bias (% per amu) for elements over the mass range from Li to U in MC-
1786 ICP-MS. The extent of the bias for an element depends primarily on its mass.

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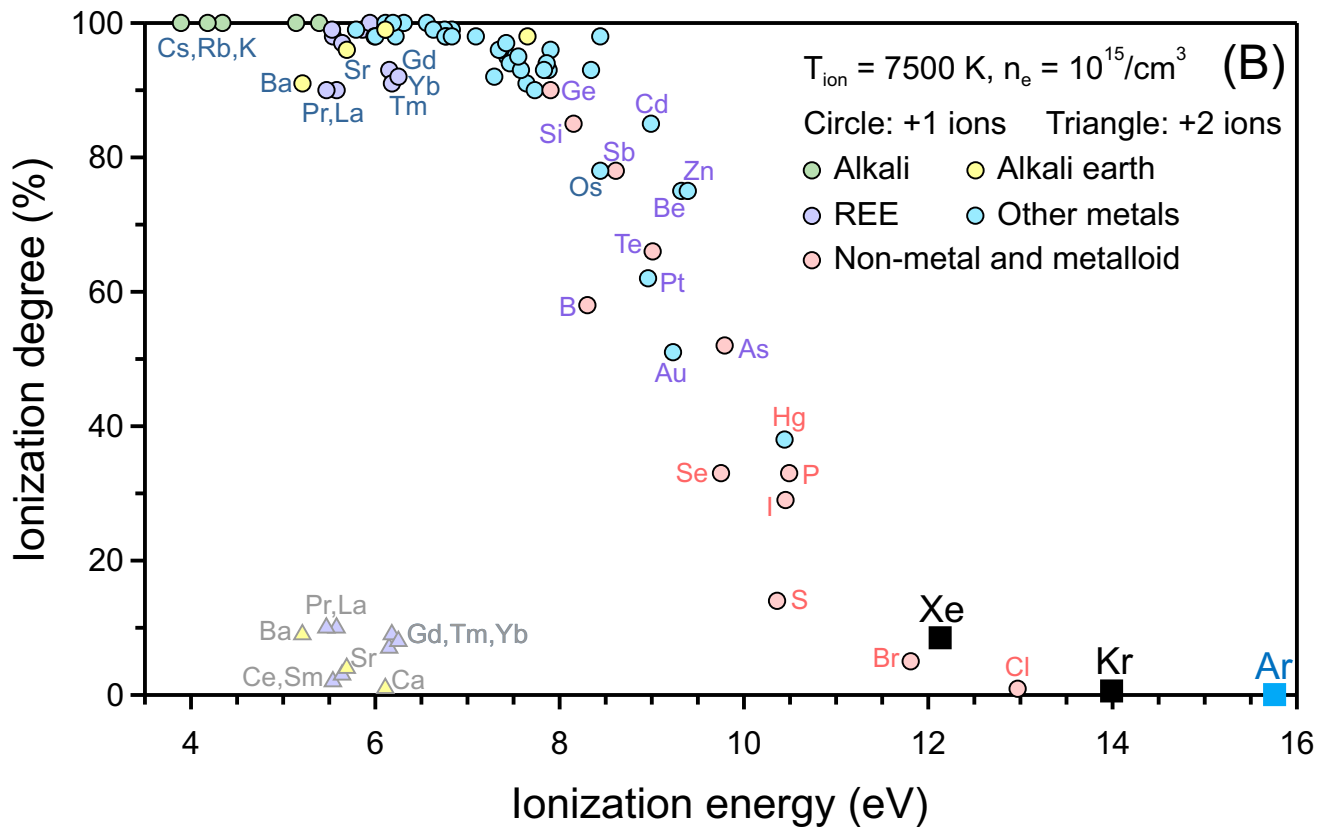
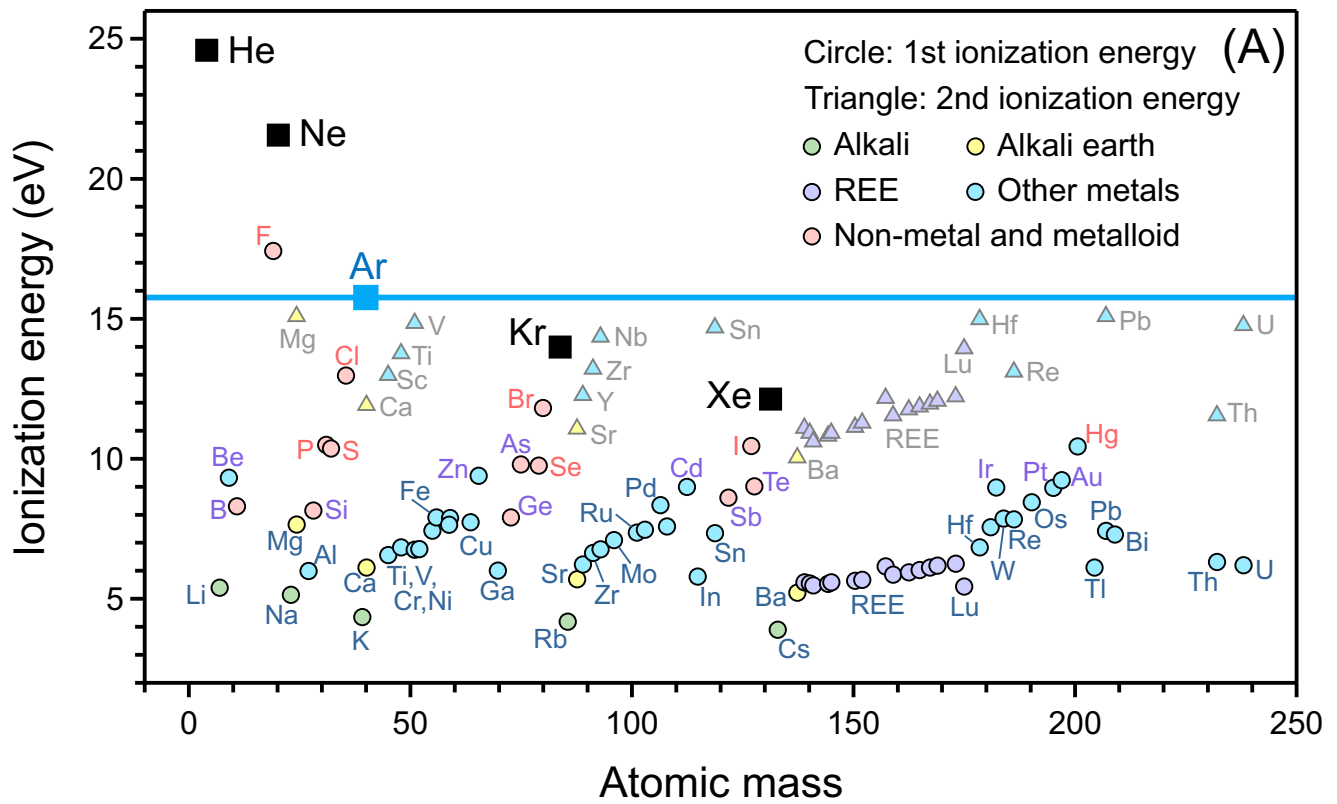


Fig. 1

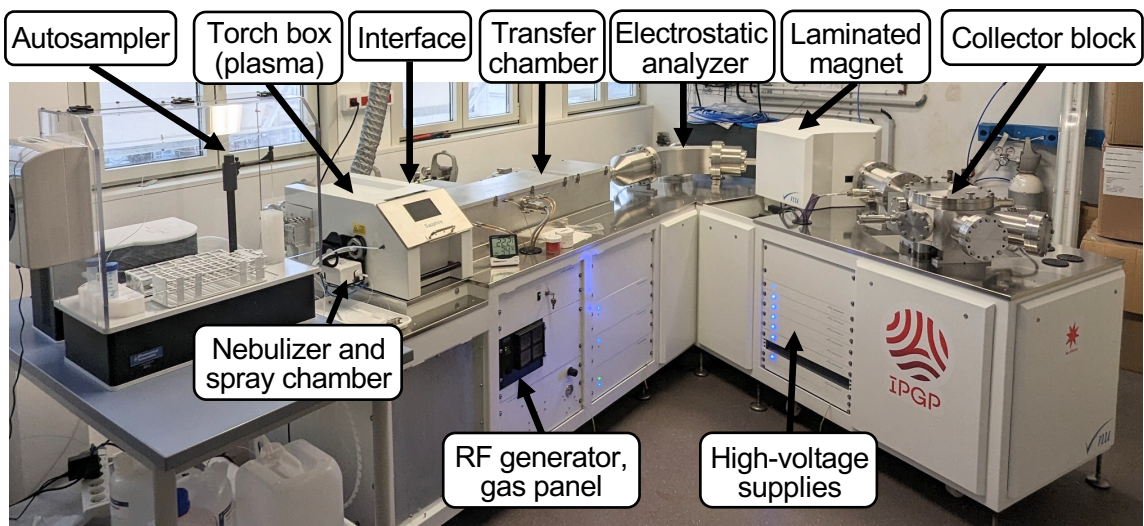
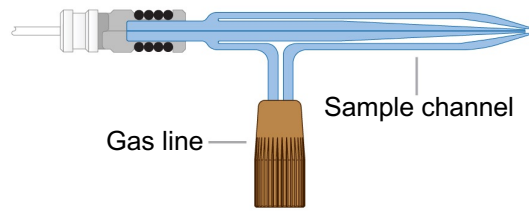
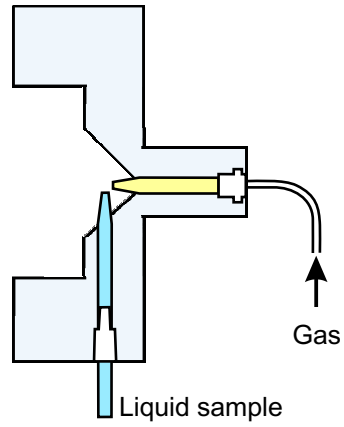


Fig. 2

(A) Concentric nebulizer



(B) Crossflow nebulizer



(C) Nebulizer transport efficiency

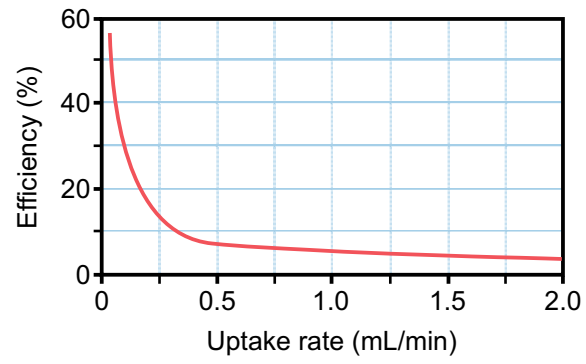
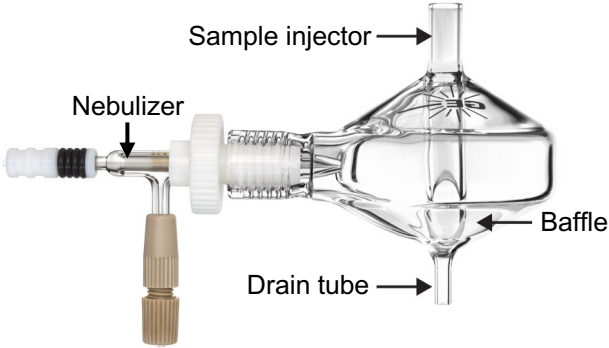


Fig. 3

(A) Cyclonic spray chamber



(B) Dual Scott/cyclonic spray chamber

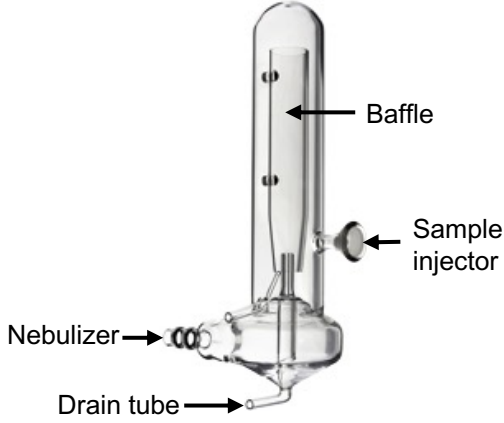
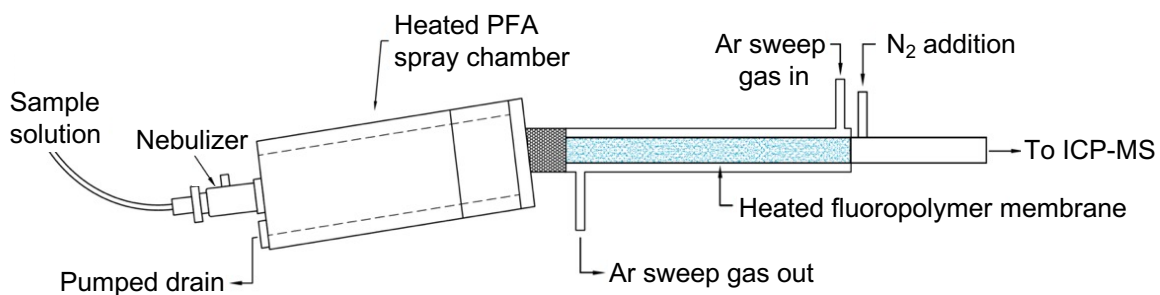


Fig. 4

(A) CETAC Aridus 3



(B) ESI Apex Omega

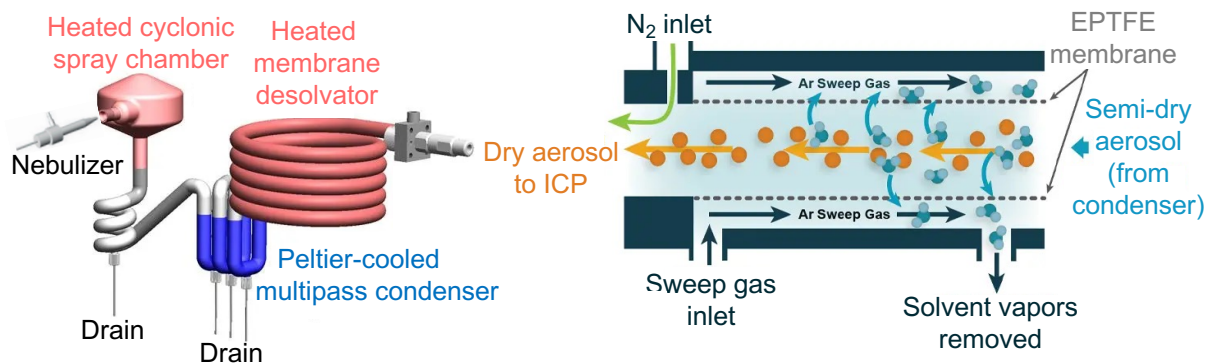


Fig. 5

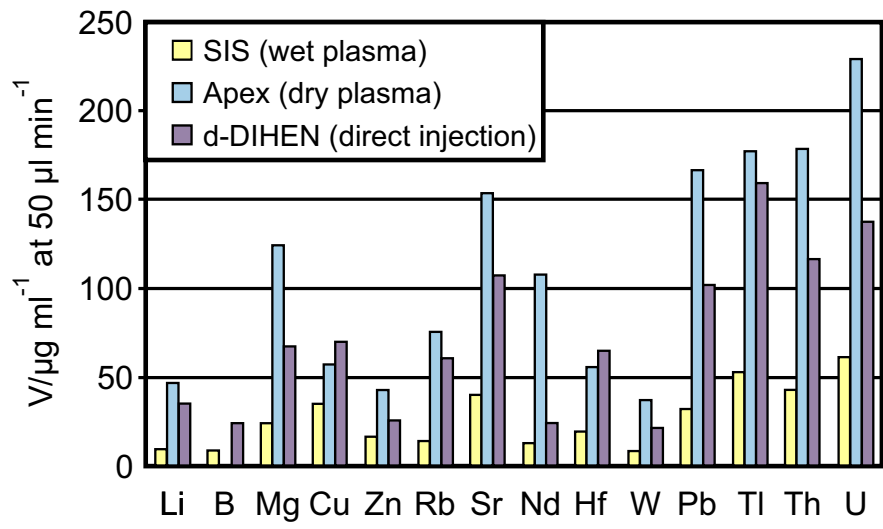
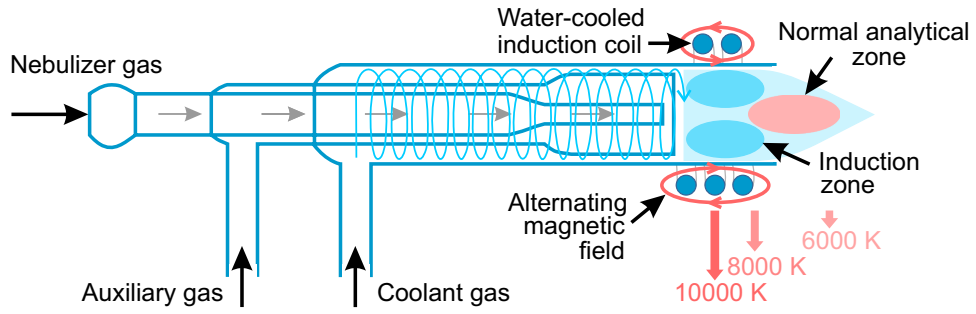


Fig. 6

(a) Torch illustration



(b) Torch box configuration

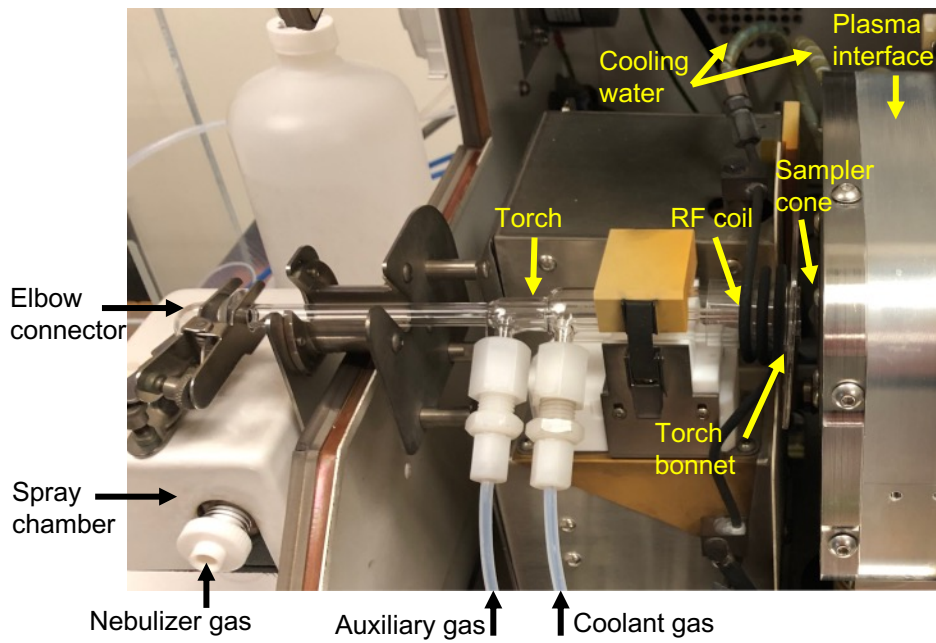
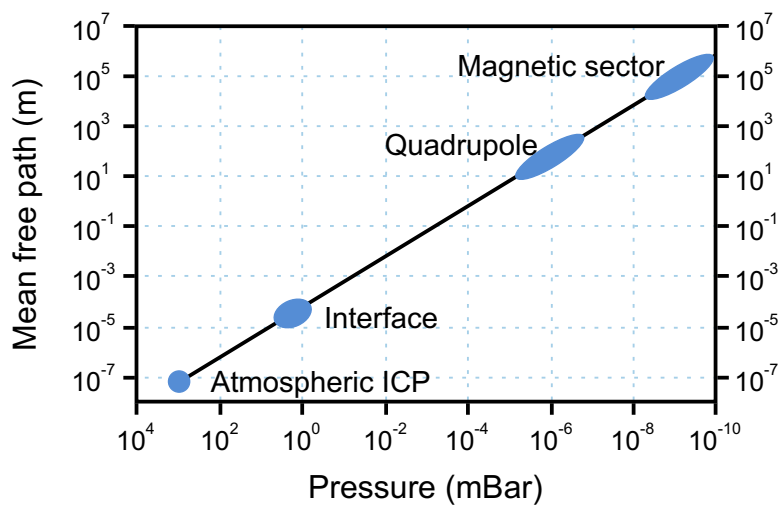


Fig. 7

(A) Pressure gradient across ICP-MS



(B) ICP-MS interface

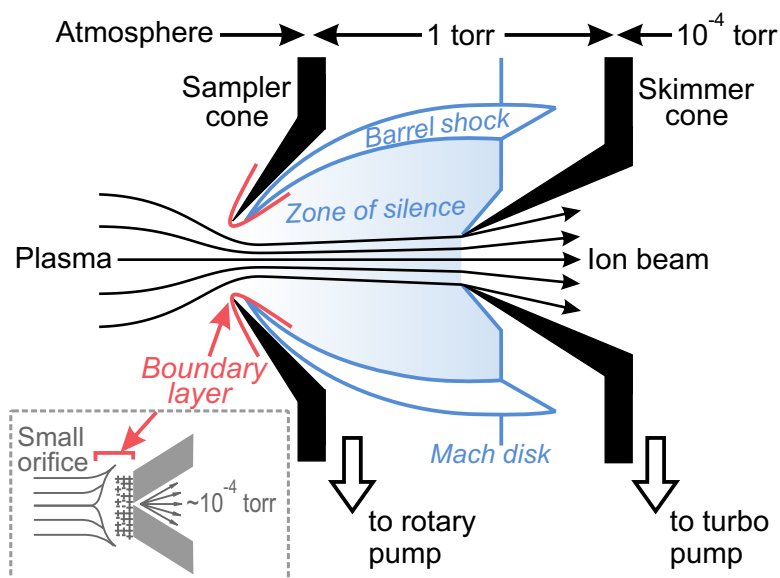
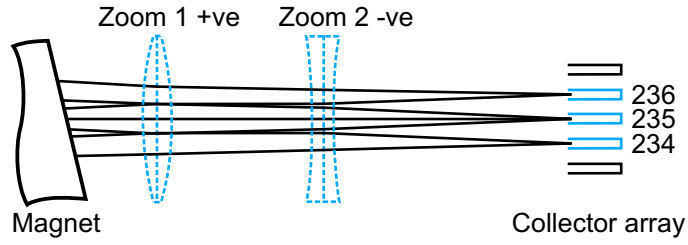
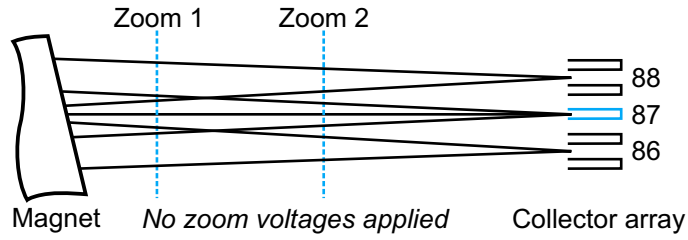


Fig. 8

(A) Increased dispersion of U isotopes



(B) Natural dispersion of Sr isotopes



(C) Adjusted dispersion of Sr isotopes

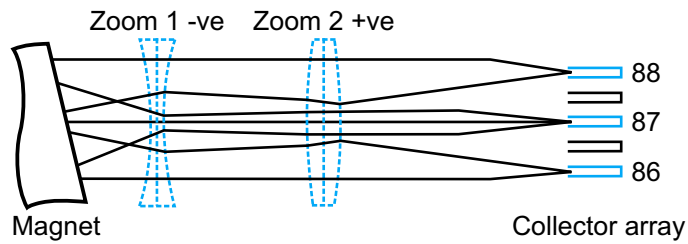


Fig. 9

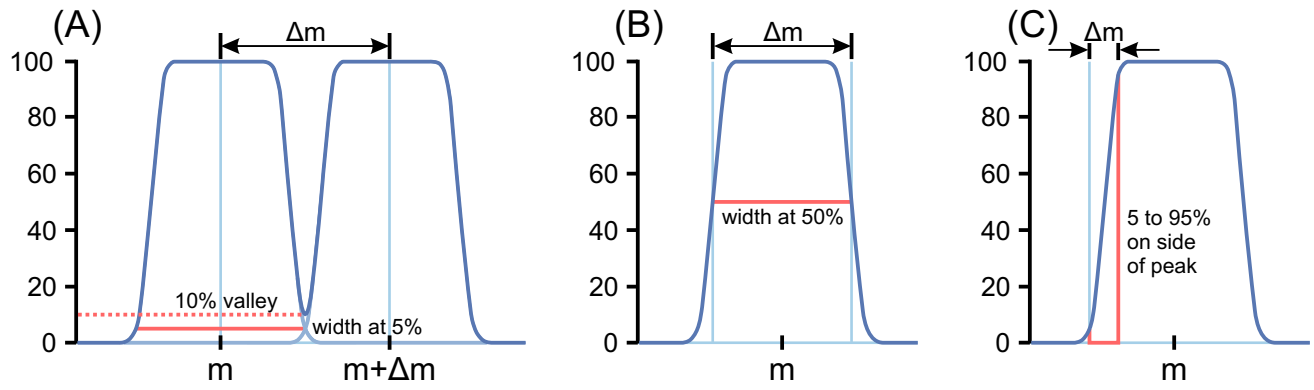


Fig. 10

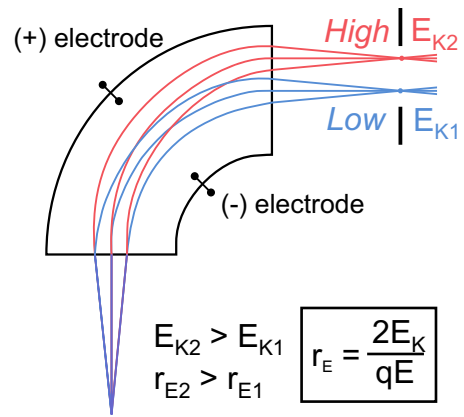


Fig. 11

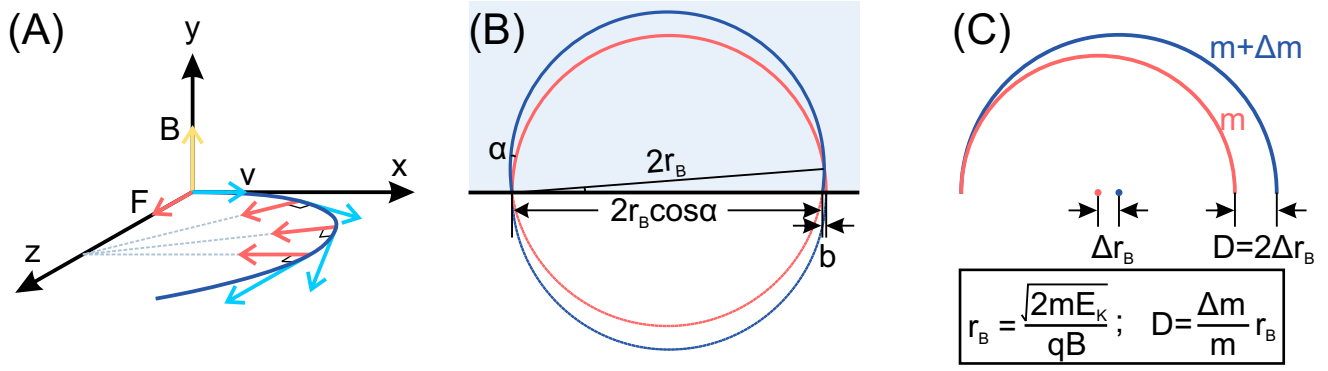


Fig. 12

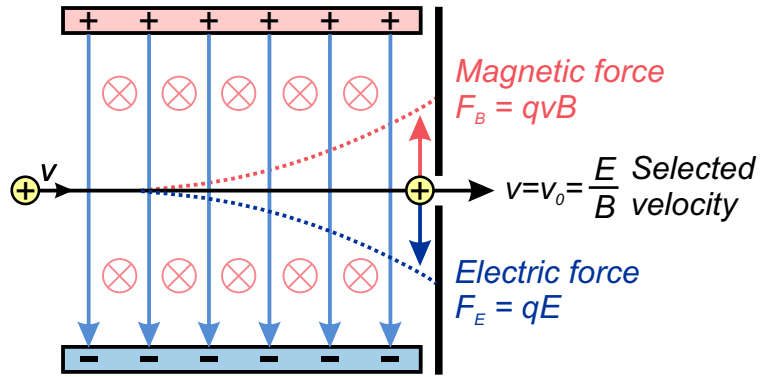
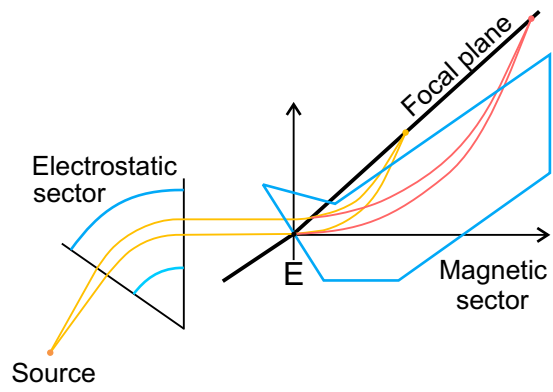


Fig. 13

(A) Mattauch-Herzog geometry



(B) Forward Nier-Johnson geometry

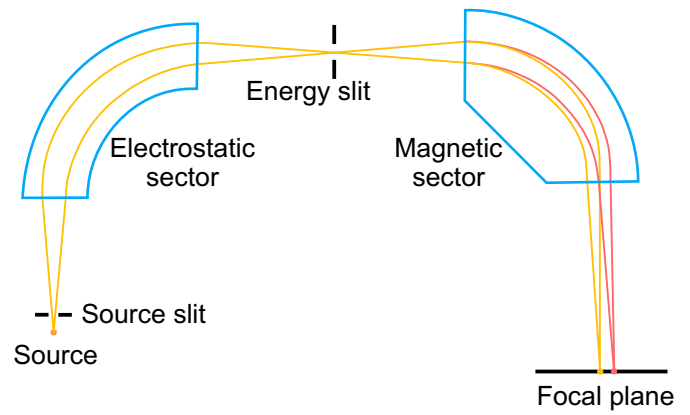


Fig. 14

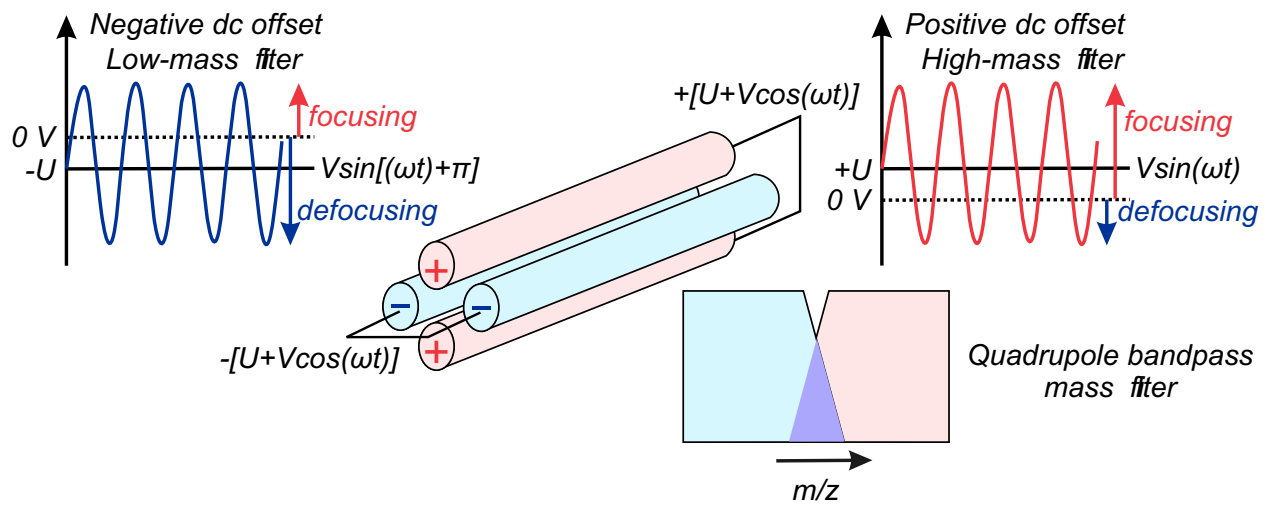


Fig. 15

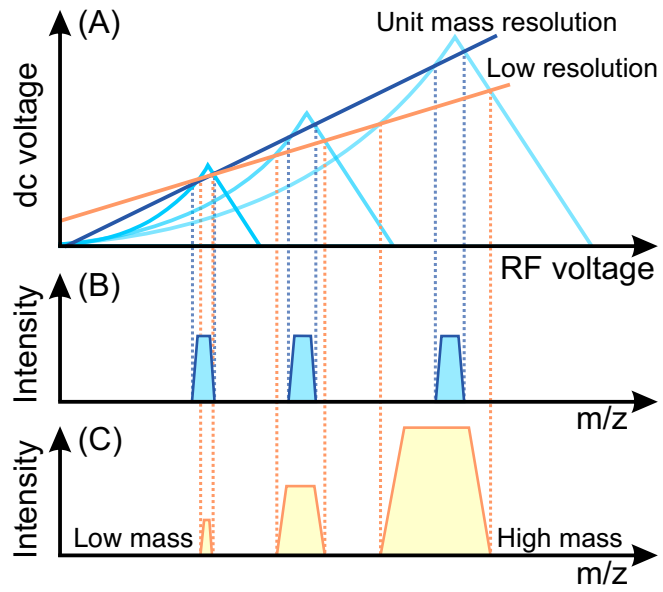


Fig. 16

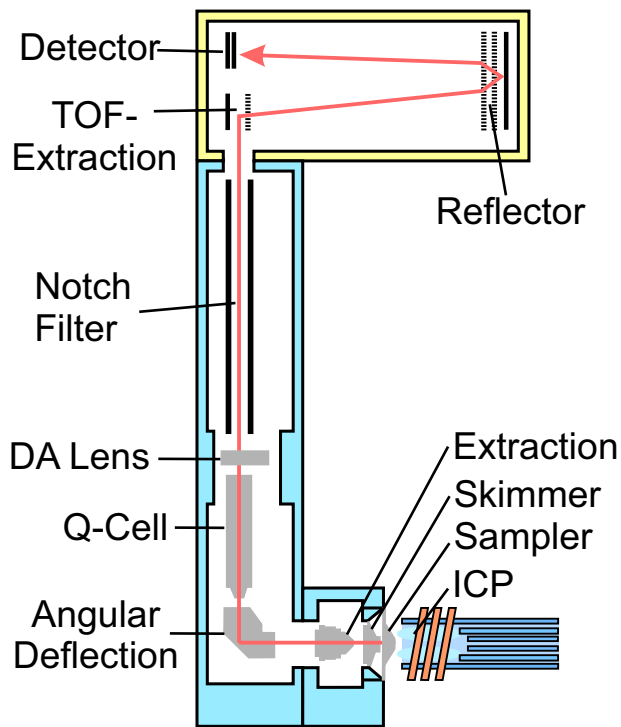


Fig. 17

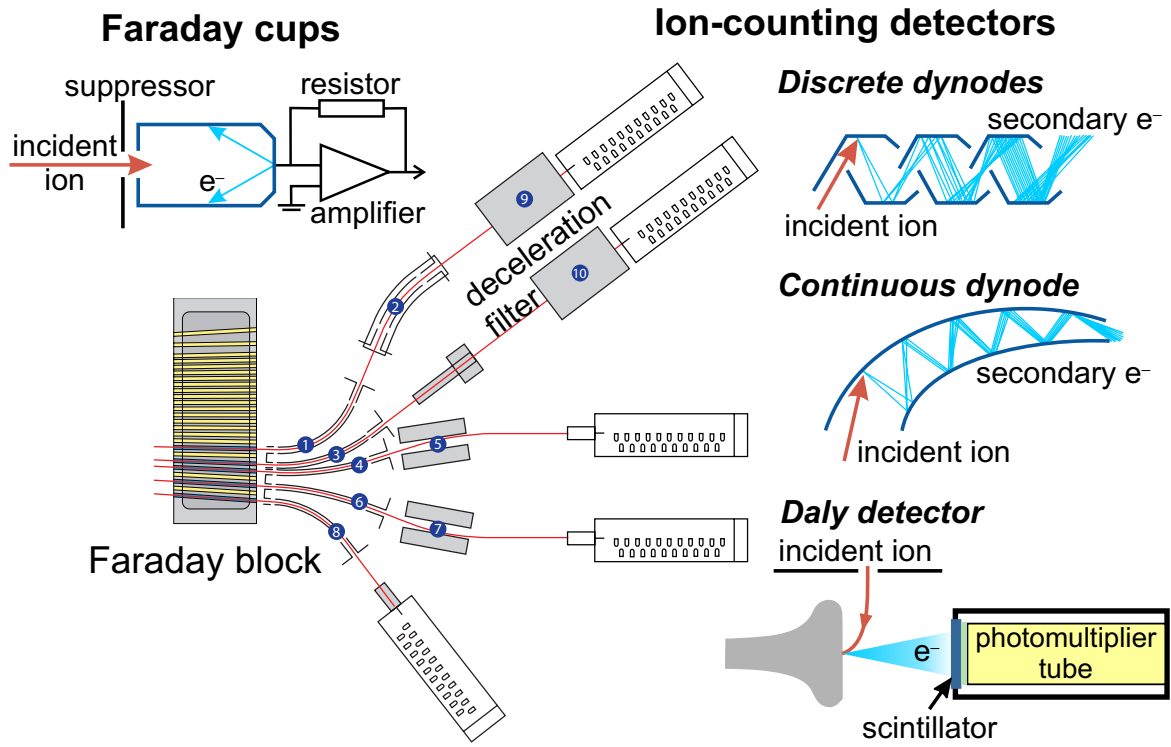


Fig. 18

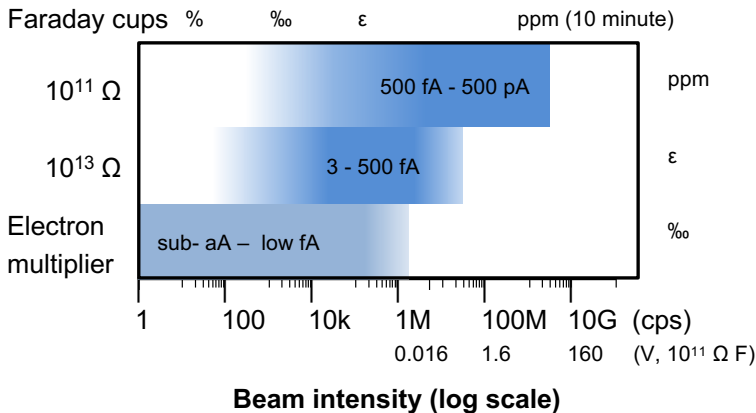


Fig. 19

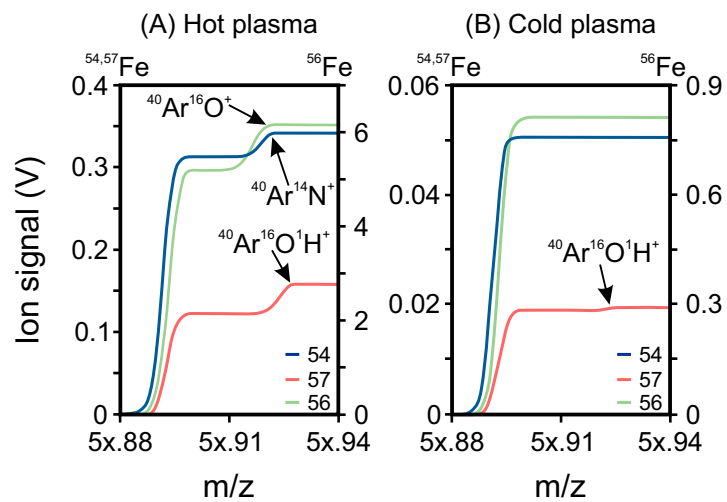


Fig. 20

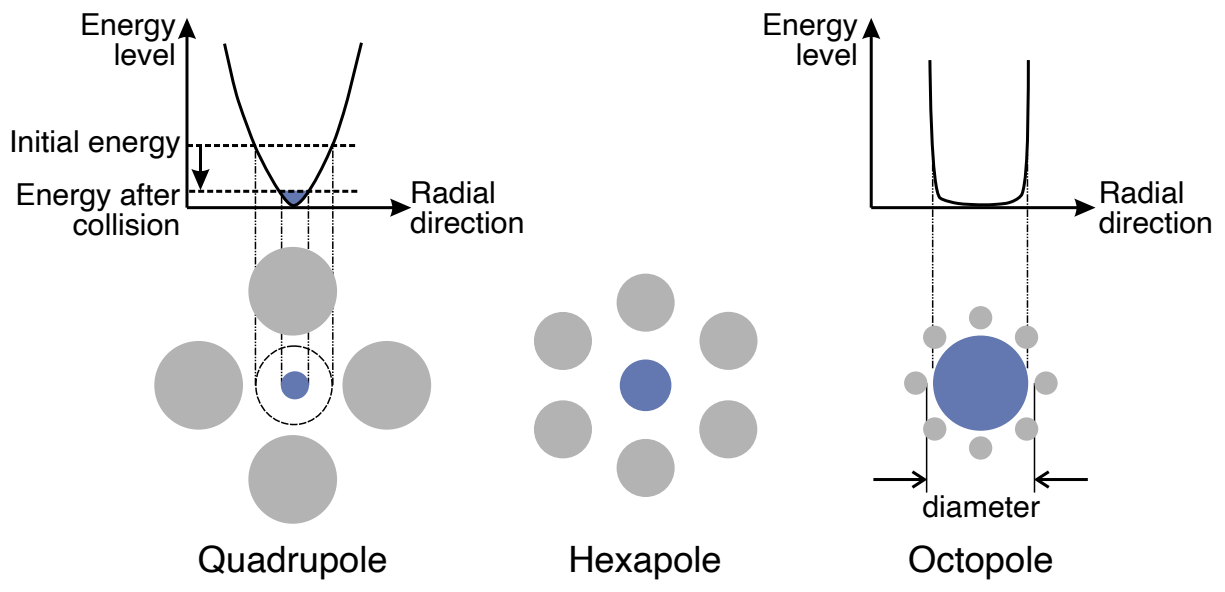


Fig. 21

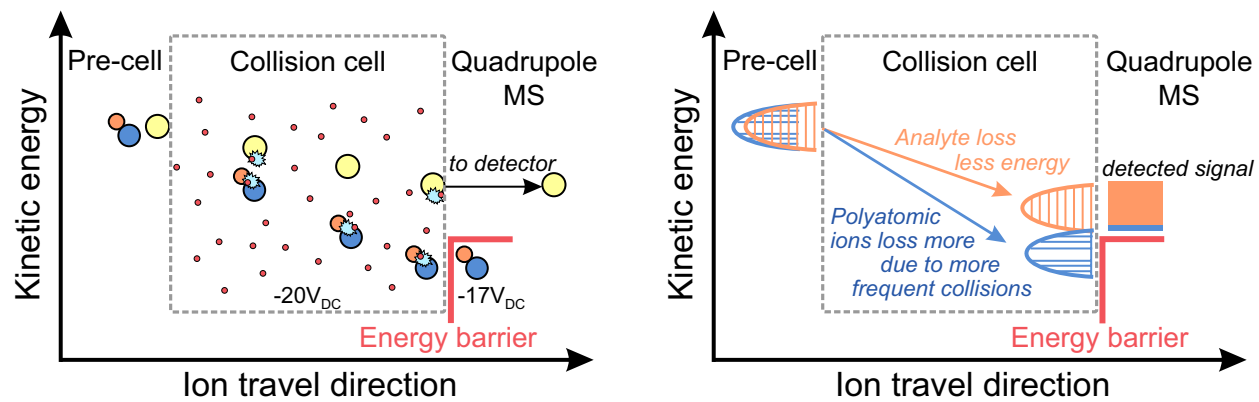
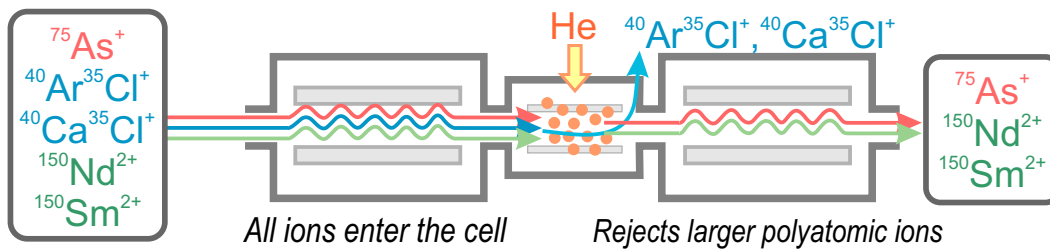
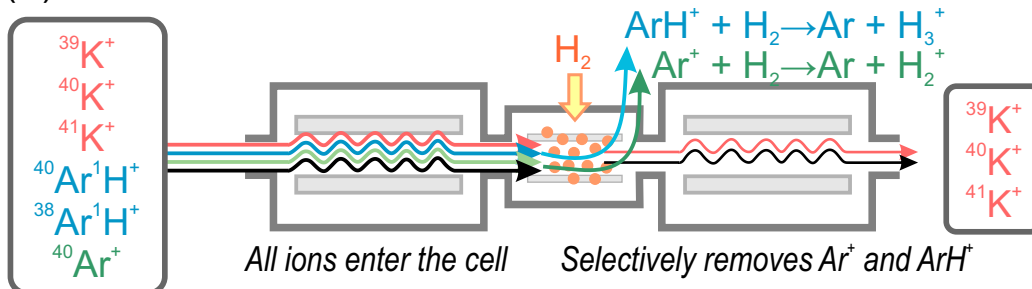


Fig. 22

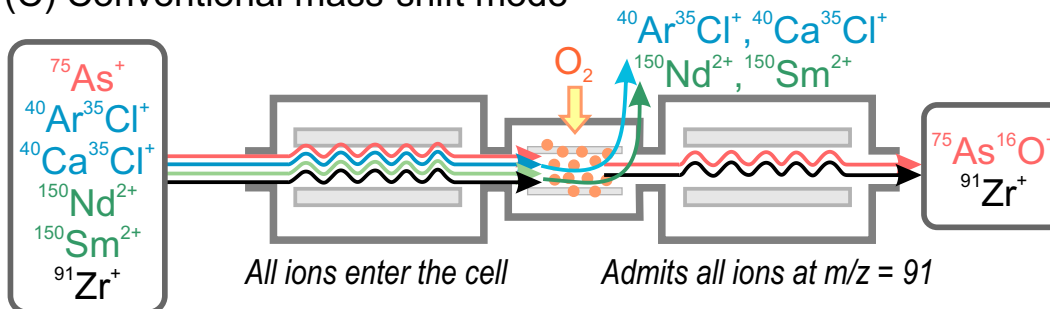
(A) Collision mode



(B) On-mass reaction mode



(C) Conventional mass-shift mode



(D) Mass-shift mode with pre-cell mass filtering

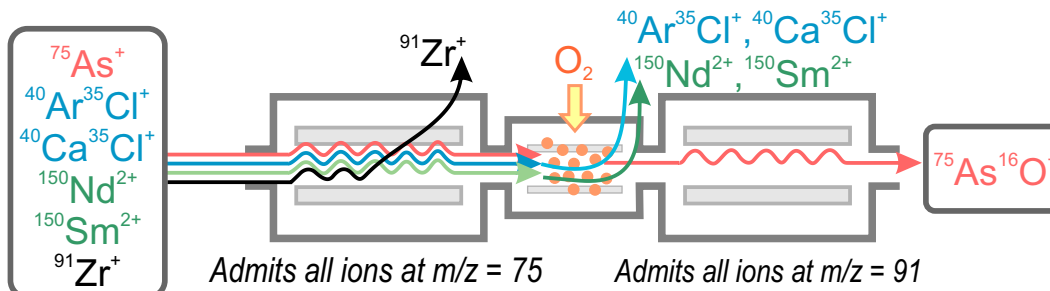


Fig. 23

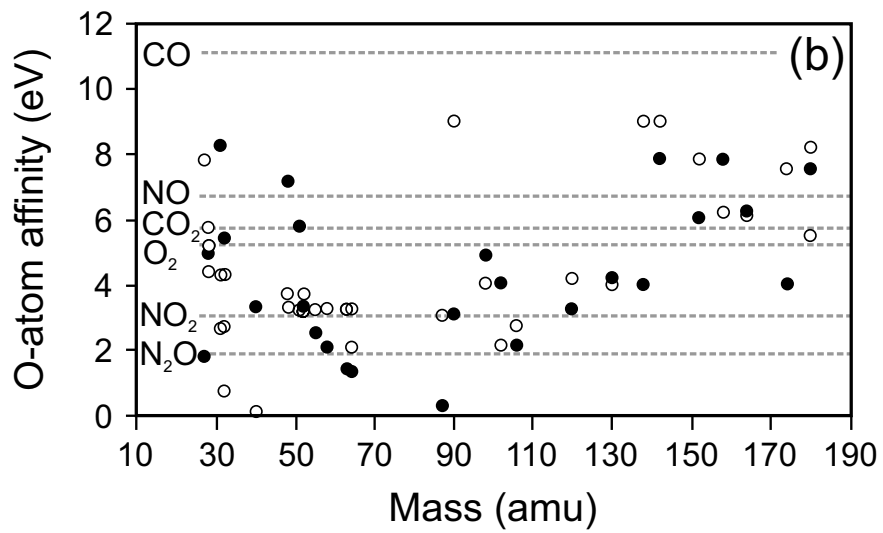
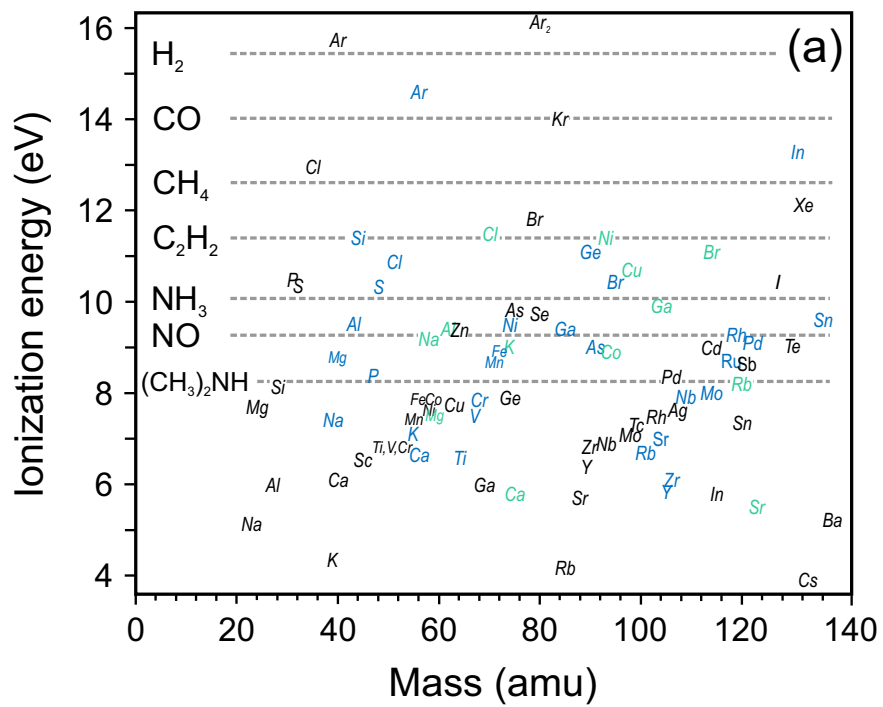


Fig. 24

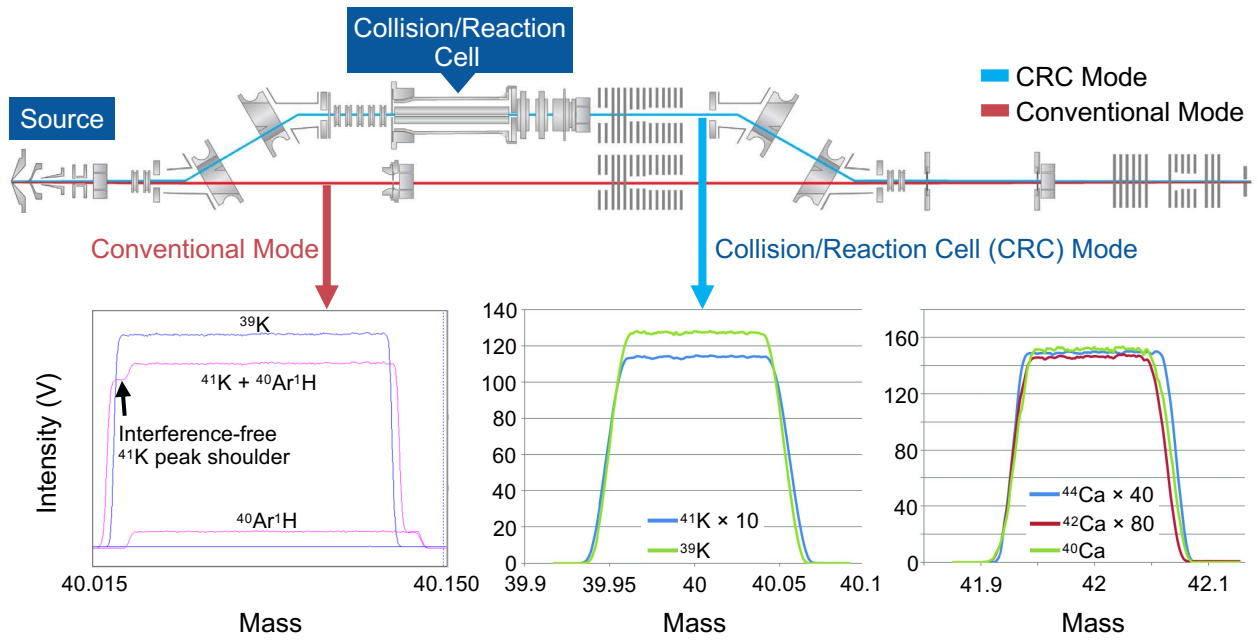
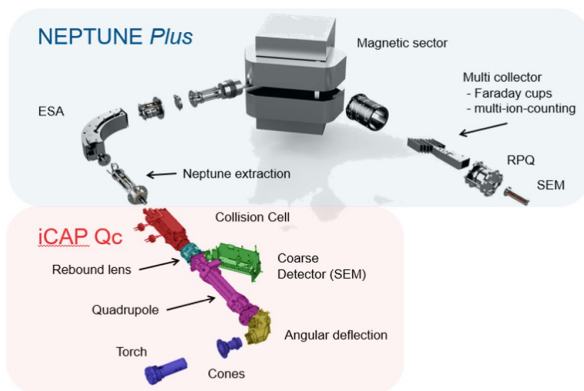
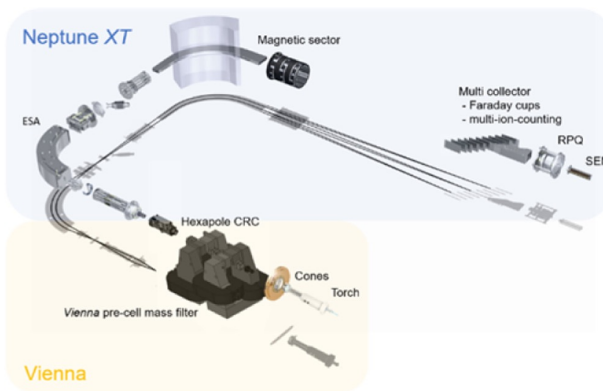


Fig. 25

(A) Prototype: Proteus



(B) Prototype: Vienna



(C) Neoma

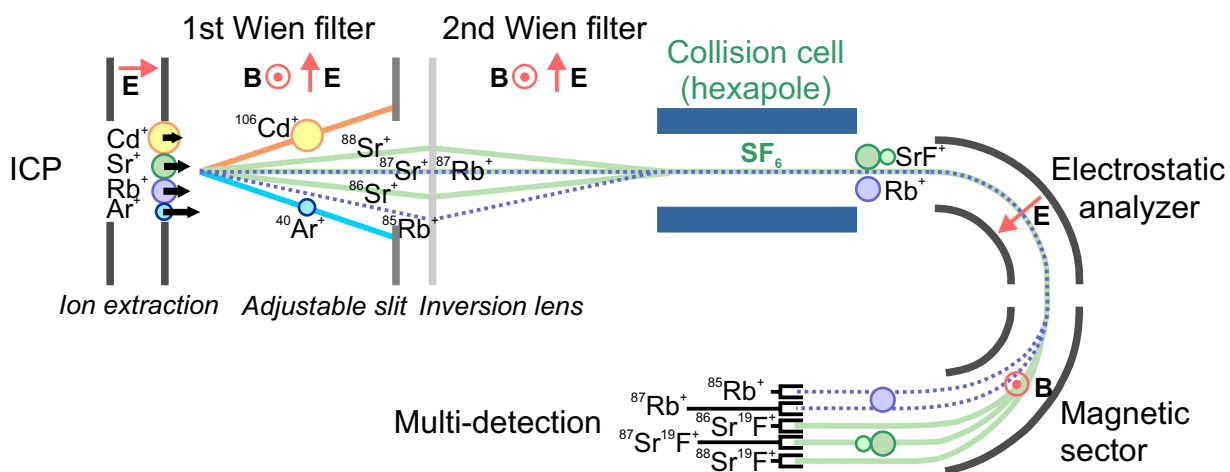


Fig. 26

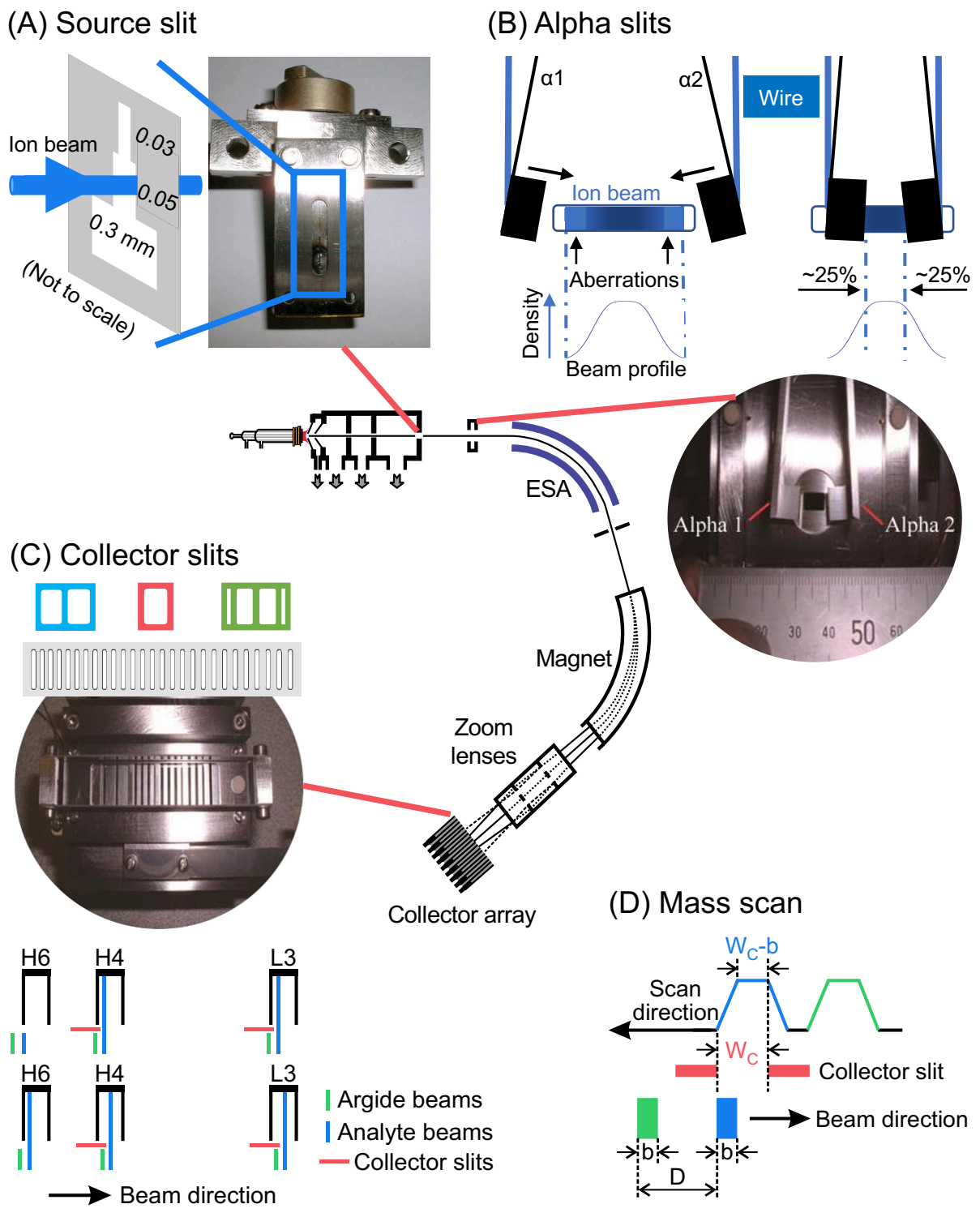


Fig. 27

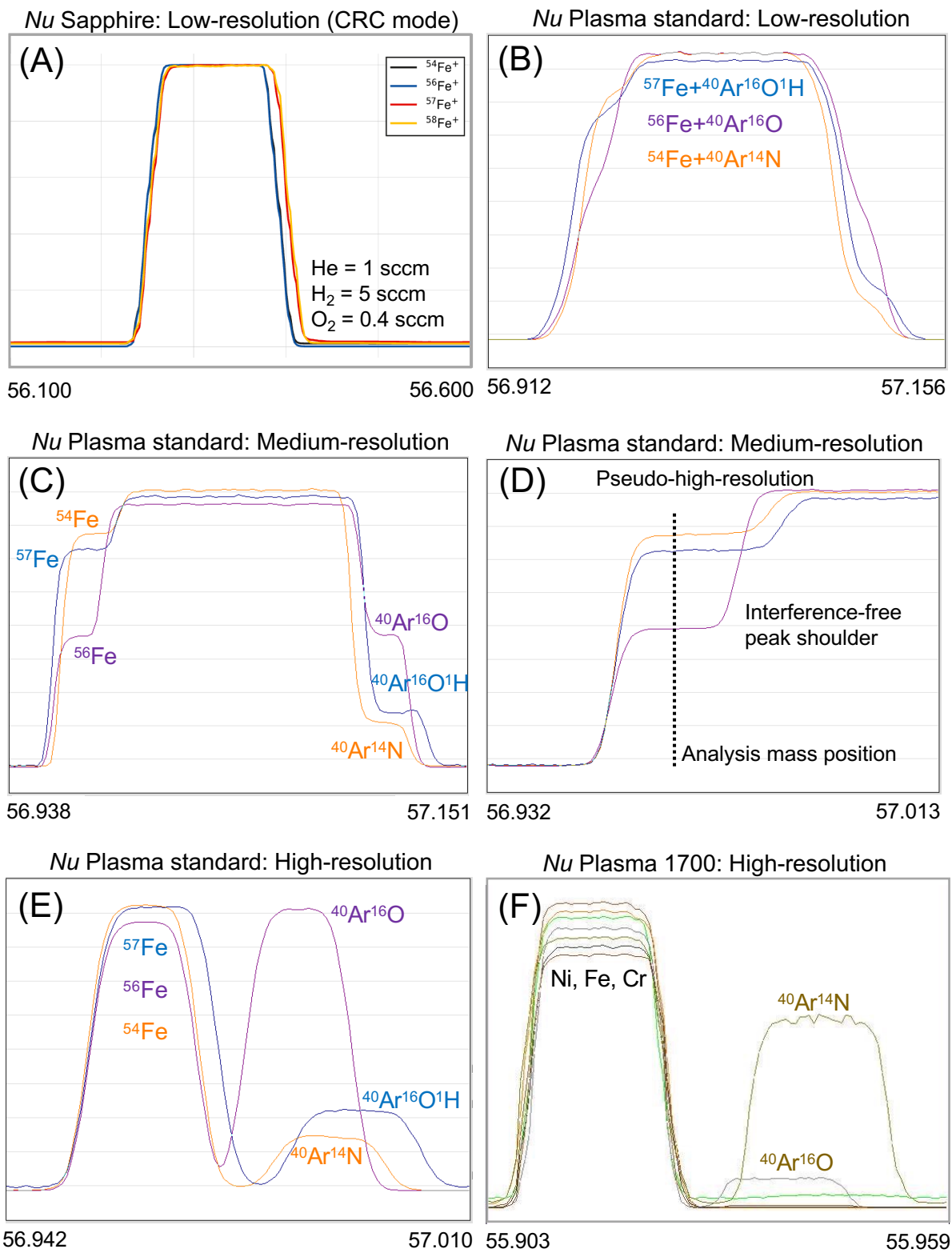


Fig. 28

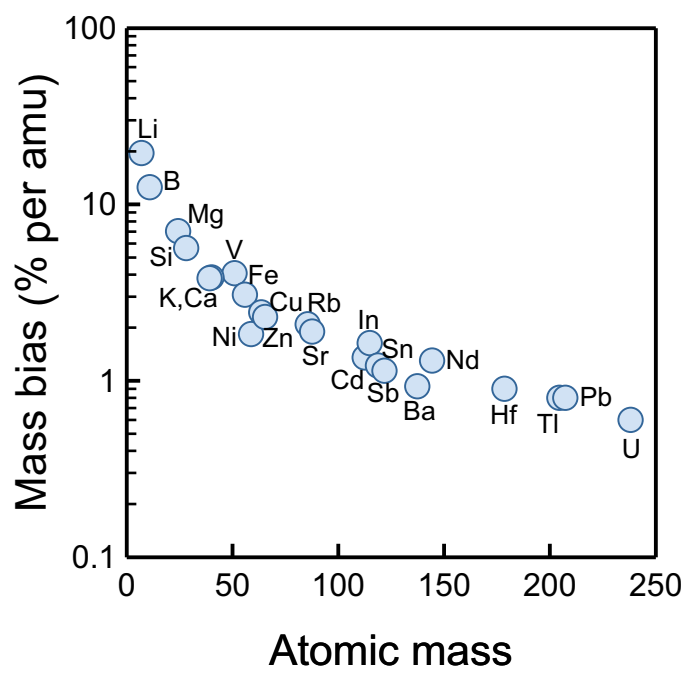


Fig. 29