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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 ( $^{20}\text{Ne}$  and  
208  $^{22}\text{Ne}$ ). 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- $\mu$ 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  $\leq 2$  (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 N<sub>2</sub> 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 HNO<sub>3</sub>). Further down-line, the acidified sample is mixed with a reducing agent (e.g., NaBH<sub>4</sub>  
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., <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup> on  
371 <sup>75</sup>As<sup>+</sup>) 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., N<sub>2</sub> and O<sub>2</sub>), 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.,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ ) (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 ( $\lambda$ ) 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  $100\lambda$  wide. The mean free path ( $\lambda = 1/n\sigma$ ) of a conventional Ar ICP is less than  $2 \times 10^{-3}$  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 ( $\lambda_D$ ), 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 ( $\sim 0.41$  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  $x = 0.5D_0$  downstream of the sampler, and reaches terminal speed ( $u = (5kT_0/m)^{0.5}$   
509  $= 2.5 \times 10^5$  cm/s) at  $x \geq 2D_0$ . Assuming the plasma expands from atmospheric pressure ( $P_0$ ) into a  
510 background pressure ( $P_1$ ) of  $\sim 2$  Torr, the shock wave terminates at the Mach disk located at  $x_m =$   
511  $0.67D_0(P_0/P_1)^{0.5} = 13$  mm. The skimmer is typically placed before the Mach disk at  $\sim 2/3x_m$  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  $\mu$ 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  $\lambda_D$  from  $\sim 10^{-4}$  mm at the sampler to  $10^{-3}$ - $10^{-2}$  mm  
516 at the skimmer tip,  $\lambda_D$  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  $\lambda_D$  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  $\sim 2500$  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 ( $\sim 300$  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  $\sim 500$  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  $\sim 5.8$  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 ( $\Delta m$ ), 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  $1.67 \times 10^{-27}$  kg and a charge of  $1.6 \times 10^{-19}$  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  $\alpha$ , 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  $2\alpha$  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<sub>B</sub>) 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<sub>B</sub> 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  $\sim 15$ . 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  $180^\circ$  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  $31.82^\circ$  electric sector followed by a  $90^\circ$  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  $90^\circ$  electric sector  
752 and a  $60^\circ$  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 ( $\sim 300$  to  
758 over 10,000) for resolving isobaric interferences from analyte ions. This resolution is a significant  
759 improvement over quadrupole-based instruments ( $\sim 300$ -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  $180^\circ$  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  $\omega$  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  $10^{-19} \text{ A}$  and  $10^{-13} \text{ A}$ ), whereas  
929 Faraday cups are preferable for higher ion beams (e.g., between  $10^{-15} \text{ A}$  and  $10^{-9} \text{ A}$ ) 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  $1.6 \times 10^{-19}$  coulomb strike the collector per second, together they deliver a beam current  
973 of  $1.6 \times 10^{-11}$  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  $\text{Ar}^+$ ,  $\text{Ar}_2^+$ , and argides.  
1032 Argon has three naturally occurring isotopes:  $^{36}\text{Ar}$  (0.337%),  $^{38}\text{Ar}$  (0.063%), and  $^{40}\text{Ar}$  (99.6%).  
1033  $^{40}\text{Ar}$  is a severe isobaric interference on  $^{40}\text{K}$ , a minor isotope of K (0.0117%). It also interferes  
1034 with  $^{40}\text{Ca}$  (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 ( $^{80}\text{Se}$ ). 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 ( $^{52}\text{Cr}$ ), and  $^{40}\text{Ar}^{14}\text{N}$  may interfere  
1042 with  $^{54}\text{Cr}$ .

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  $^1\text{H}$ ,  $^{16}\text{O}$ , 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  $^{46}\text{Ti}$  (7.99%),  $^{47}\text{Ti}$  (7.32%),  $^{48}\text{Ti}$  (73.98%),  $^{49}\text{Ti}$  (5.46%), and  $^{50}\text{Ti}$  (5.25%). Their oxides form  
1049 interferences on  $^{62}\text{Ni}$  ( $^{46}\text{Ti}^{16}\text{O}$ ),  $^{63}\text{Cu}$  ( $^{47}\text{Ti}^{16}\text{O}$ ),  $^{64}\text{Zn}$  ( $^{48}\text{Ti}^{16}\text{O}$ ),  $^{65}\text{Cu}$  ( $^{49}\text{Ti}^{16}\text{O}$ ), and  $^{66}\text{Zn}$  ( $^{50}\text{Ti}^{16}\text{O}$ ).  
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 HNO<sub>3</sub> 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 <sup>75</sup>As (overlapping with <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup>), and for V,  
1083 which has its dominant isotope (<sup>51</sup>V) overlapping with <sup>35</sup>Cl<sup>16</sup>O<sup>+</sup>. Sulfuric acid and H<sub>3</sub>PO<sub>4</sub> are  
1084 generally not recommended because they can form a variety of S- and P-bearing polyatomic ions.  
1085 For example, <sup>32</sup>S<sup>16</sup>O<sup>+</sup> and <sup>31</sup>P<sup>16</sup>O<sup>1</sup>H<sup>+</sup> are direct interferences on <sup>48</sup>Ti<sup>+</sup>, and <sup>32</sup>S<sup>16</sup>O<sub>2</sub><sup>+</sup> is a direct  
1086 interference on <sup>64</sup>Zn<sup>+</sup>. In addition, <sup>31</sup>P<sup>14</sup>N<sup>+</sup> interferes with <sup>45</sup>Sc, the only Sc isotope, and <sup>31</sup>P<sup>16</sup>O<sub>2</sub><sup>+</sup>  
1087 interferes with <sup>63</sup>Cu, the major Cu isotope. One effective approach to suppress hydride formation  
1088 is to replace H<sub>2</sub>O with D<sub>2</sub>O, which eliminates the major polyatomic interference of <sup>36</sup>ArH<sup>+</sup> on  
1089 <sup>37</sup>Cl<sup>+</sup>, thereby enabling the accurate determination of <sup>37</sup>Cl/<sup>35</sup>Cl 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 AgNO<sub>3</sub> 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  $\text{CeO}^+/\text{Ce}^+$ , 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  $\text{N}_2$ , 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- $\text{N}_2$  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  $\text{Ar}^+$ , or they can enhance the ionization of analyte elements by Penning

1122 ionization (Boumans and De Boer 1977). In an Ar-N<sub>2</sub> plasma, the energy of the lower metastable  
1123 level of Ar atoms is slightly higher than the excitation of vibrational levels of N<sub>2</sub> molecules by  
1124 electron impact. This leads to efficient collisional energy transfer that quenches the metastable Ar  
1125 by exciting the vibrational levels of N<sub>2</sub> 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 N<sub>2</sub>, N<sub>2</sub><sup>+</sup>, and N<sup>+</sup> species are highly active in scavenging O<sub>2</sub> to form NO<sup>+</sup>. Based on  
1128 ion distributions measured in a mixed Ar-N<sub>2</sub> plasma, ionization is suggested to occur primarily by  
1129 charge transfer with NO<sup>+</sup>, N<sub>2</sub><sup>+</sup>, or Ar<sup>+</sup> (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-N<sub>2</sub>  
1132 plasma where ionization is dominated by charge transfer with NO<sup>+</sup>. Adding low-flow of N<sub>2</sub> (30  
1133 mL/min, < 5% vol./vol.) to the nebulizer gas has been shown to considerably reduce the formation  
1134 of ArCl<sup>+</sup>, ArAr<sup>+</sup>, and ArO<sup>+</sup>, 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<sup>+</sup> is lower than that for most Ar- and Cl-based polyatomic interferences, which limits their  
1137 production in an Ar-N<sub>2</sub> plasma. The formation of NO<sup>+</sup> 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<sup>+</sup> (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-N<sub>2</sub> 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 N<sub>2</sub> 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 N<sub>2</sub> has a higher thermal conductivity than Ar, the presence of N<sub>2</sub> may lead to enhanced energy  
1149 transfer from the toroidal region of the plasma to its central channel. However, N<sub>2</sub> molecules also  
1150 absorb energy, which results in the cooling of the central channel. Therefore, the amount of N<sub>2</sub>  
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 N<sub>2</sub>. In contrast, high flow rates of N<sub>2</sub> can  
1154 lead to signal reduction or even plasma extinction (see review by Scheffler and Pozebon 2014).

1155 The effect of N<sub>2</sub> 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<sup>+</sup> molecules in an Ar-N<sub>2</sub> 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<sup>+</sup> can enhance the ionization  
1160 of elements with relatively high ionization energies. The improved thermal conductivity in Ar-N<sub>2</sub>  
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  $\text{NO}^+$ , similar  
1171 to that in a mixed Ar- $\text{N}_2$  plasma (Tanner 1995; Holliday and Beauchemin 2002). Therefore, when  
1172 using cold plasma, especially with a desolvation nebulization system,  $\text{NO}^+$  becomes the  
1173 predominant background species, while  $\text{Ar}^+$ ,  $\text{ArO}^+$ , and  $\text{ArH}^+$  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 ( $\text{C}_2^+$ ,  $\text{C}_2\text{H}^+$ ,  $\text{C}_2\text{H}_2^+$  and  $\text{CN}^+$ ) 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.,  $\text{ArO}^+$ ) 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  $\text{Ce}^+$   
1224 reacted with  $\text{O}_2$  much more efficiently than  $\text{CeO}^+$  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  $\text{Ar}_2^+$ ,  $\text{ArO}^+$ , and  $\text{ArN}^+$  when Xe or  $\text{CH}_4$  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 ( $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{CH}_4$ ) 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.,  $\text{NH}_3$  and  $\text{CH}_4$ ) to induce abundant ion-molecule interactions. In comparison, lighter  
1247 gases (e.g., He and  $\text{H}_2$ ) 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., H<sub>2</sub>), 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 <sup>75</sup>As<sup>+</sup> as <sup>75</sup>As<sup>16</sup>O<sup>+</sup>). In mass-shift mode, it is  
1269 possible that certain matrix elements in the sample (e.g., <sup>91</sup>Zr<sup>+</sup>) form isobaric interferences with  
1270 the product molecular ions (<sup>75</sup>As<sup>16</sup>O<sup>+</sup>, 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<sup>+</sup>, ArO<sup>+</sup>, ArCl<sup>+</sup>, and ArH<sup>+</sup>). 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<sup>+</sup>, 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 H<sub>2</sub> to Ar<sup>+</sup> (e.g., Ar<sup>+</sup> + H<sub>2</sub> → Ar + H<sub>2</sub><sup>+</sup>), freeing m/z = 40 for the  
1282 measurement of <sup>40</sup>Ca<sup>+</sup>.

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<sup>+</sup> + B → BH<sup>+</sup> +A),  
1285 hydrogen atom transfer (A<sup>+</sup> + BH → AH<sup>+</sup> +B), and hydride ion transfer (A<sup>+</sup> + BH → B<sup>+</sup> +AH)  
1286 due to the fast reaction rate of small-sized hydrogen (Tanner et al., 2002). For instance, ArO<sup>+</sup> and  
1287 ArOH<sup>+</sup> have lower ionization energies than H<sub>2</sub>, so they cannot be neutralized by charge transfer  
1288 with H<sub>2</sub>. Instead, these interferences can be removed through successive exothermic reactions of  
1289 ArO<sup>+</sup> + H<sub>2</sub> → ArOH<sup>+</sup> + H and ArOH<sup>+</sup> + H<sub>2</sub> → H<sub>2</sub>O<sup>+</sup> + Ar + H (Arnold et al., 2008). Another  
1290 example is the proton transfer reaction of ArH<sup>+</sup> + H<sub>2</sub> → H<sub>3</sub><sup>+</sup> +Ar to remove ArH<sup>+</sup>, which is a major  
1291 interference on <sup>41</sup>K<sup>+</sup> (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 N<sub>2</sub>O and CO<sub>2</sub> have  
1298 the advantage of forming stable reaction products (e.g., N<sub>2</sub> and CO). In comparison, targeted  
1299 oxidation of specific ions can be achieved by reactions with O<sub>2</sub> or NO, which require strong A<sup>+</sup>-O  
1300 bonding. Exothermic oxidation by O<sub>2</sub> has facilitated the measurement of S and P concentrations  
1301 by converting them to SO<sup>+</sup> and PO<sup>+</sup>, thereby shifting their masses away from those of polyatomic  
1302 interferences (e.g., NO<sup>+</sup>, NOH<sup>+</sup>, CH<sub>3</sub>O<sup>+</sup>, <sup>16</sup>O<sub>2</sub><sup>+</sup>) (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  $\text{SrF}^+$  by F-atom transfer with  $\text{CH}_3\text{F}$  and  $\text{SF}_6$ ,  $\text{SrCl}^+$  by Cl-atom transfer  
1308 with  $\text{CH}_3\text{Cl}$ , and  $\text{SrO}^+$  by O-atom transfer with  $\text{N}_2\text{O}$ . 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  $\leq 2$  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  $^{87}\text{Rb}$ - $^{87}\text{Sr}$  measurements on minerals using  
1350  $\text{SF}_6$  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 ( $\sim 300$ - $400$ ) through medium ( $\sim 4000$ - $9000$ ) to high ( $\geq 10000$ ).  
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  $\text{Ar}_2^+$  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 ~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  $\alpha$ :

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

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  $\beta$ :

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 ( $\beta$ ) can be solved along with the isotope fractionation of a sample  
1445 relative to a reference standard ( $\alpha$ ) 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  $\beta$ , 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 ( $\beta$ ) 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,  $\beta_{Cu}$  and  $\beta_{Zn}$  could differ by 10%, while their ratio  
 1505 remain constant during an analytical session. Therefore, Maréchal et al. (1999) suggested  
 1506 calculating the  $\beta_{Cu}/\beta_{Zn}$  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  $^{40}\text{Ca}$  is directly measurable, with limited isobaric interference from  
1559  $^{40}\text{Ar}$ . 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  $^{40}\text{K}$ - $^{40}\text{Ca}$  dating (Dai  
1562 et al., 2023), to identify the presence of short-lived  $^{41}\text{Ca}$  as  $^{41}\text{K}$  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  $^4\text{He}$  (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 ( $T_{\text{ion}}$ ) 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  $^{57}\text{Fe}$ . 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  $\text{H}_2$

1734 remove  $40\text{Ar}^+$  and  $\text{ArH}^+$  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  $\text{O}_2$  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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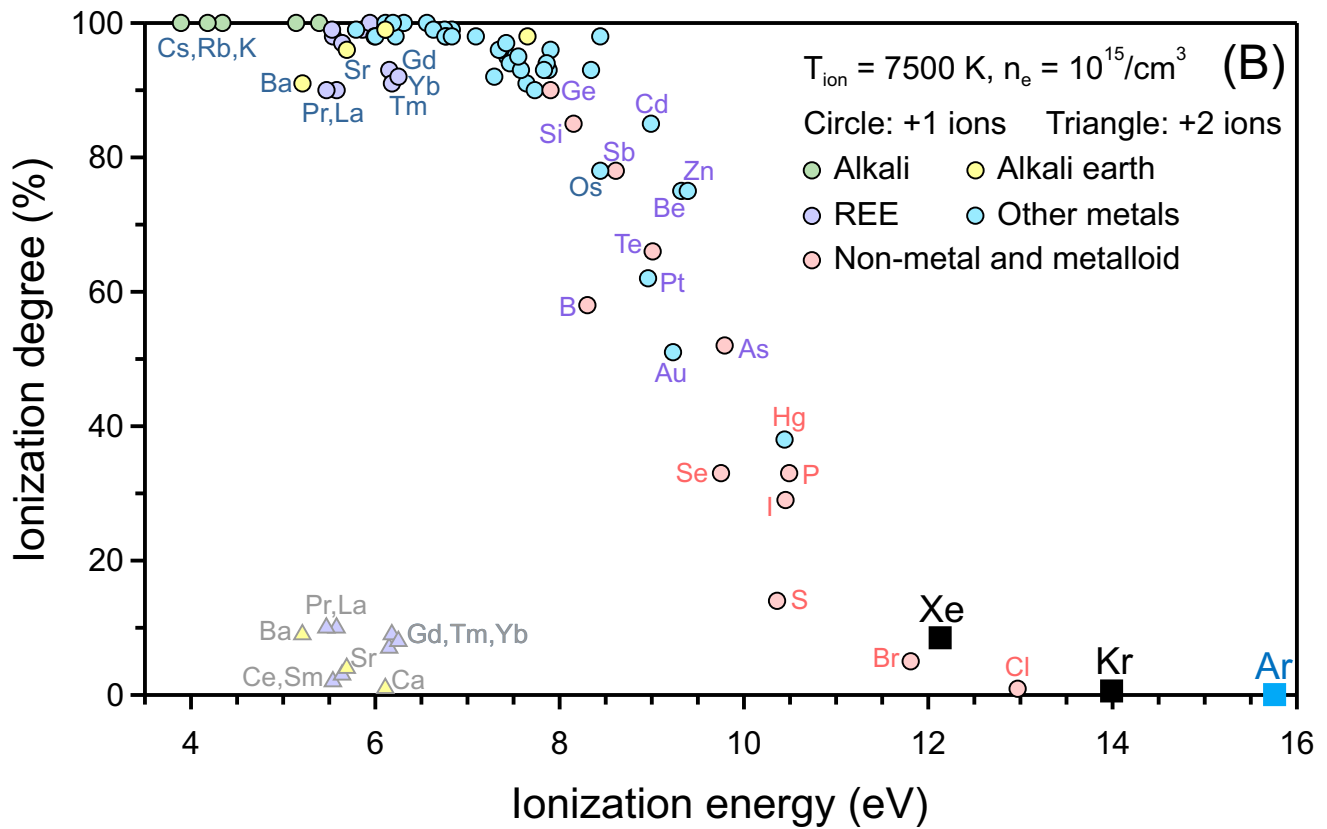
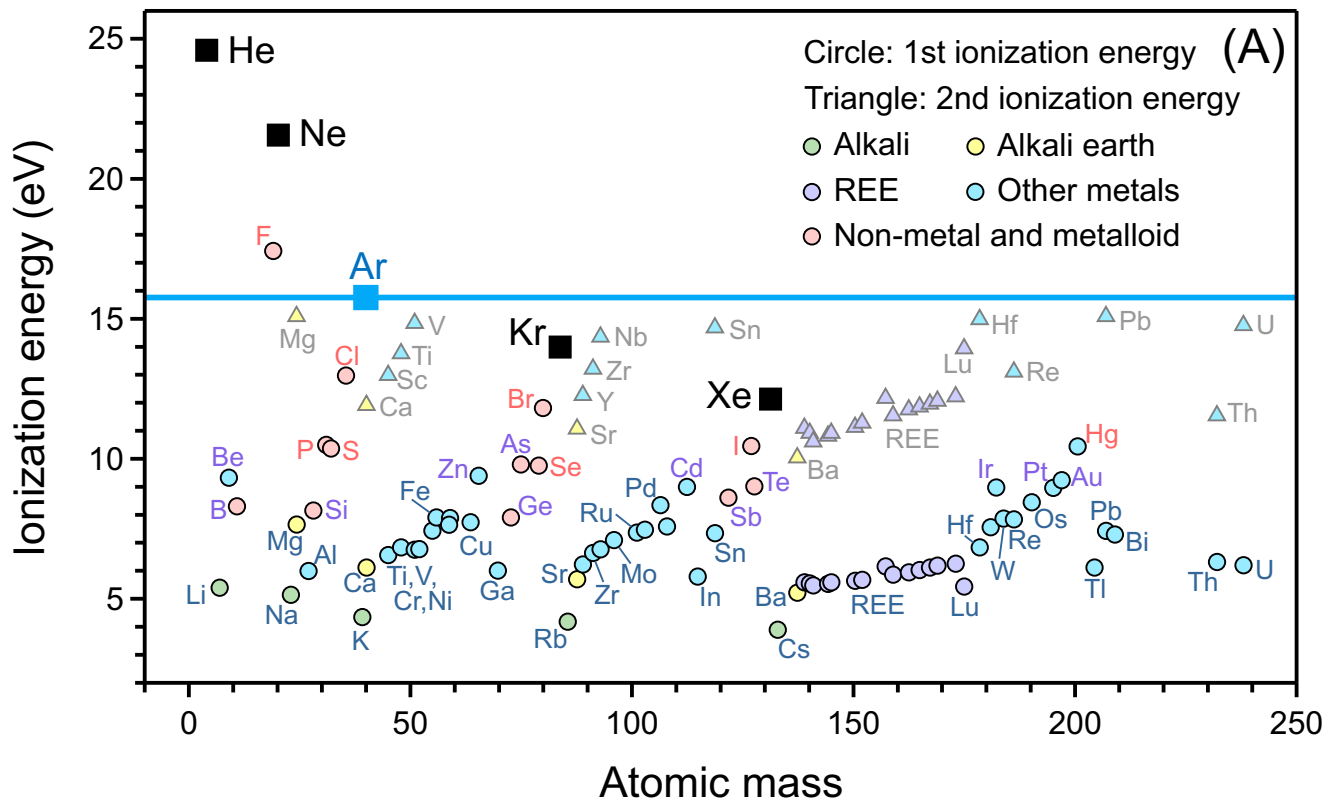
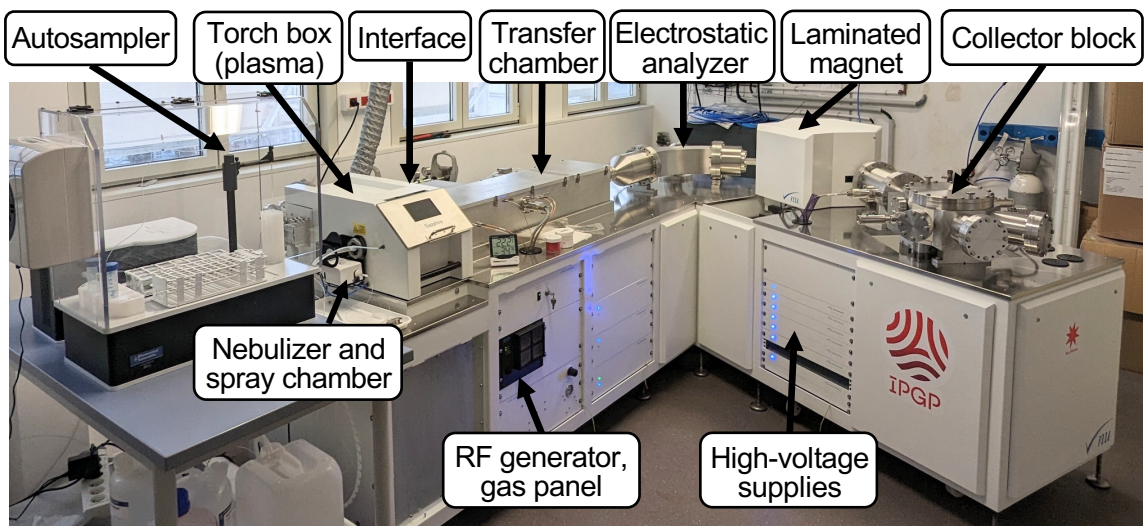
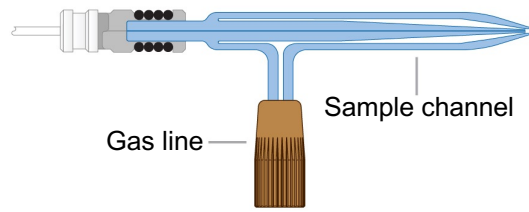


Fig. 1

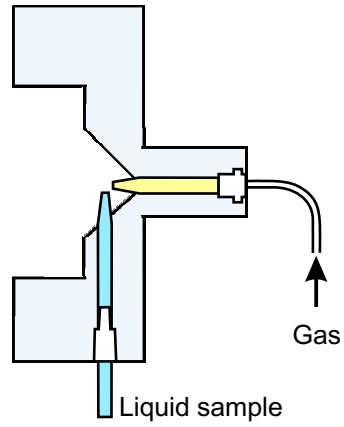


**Fig. 2**

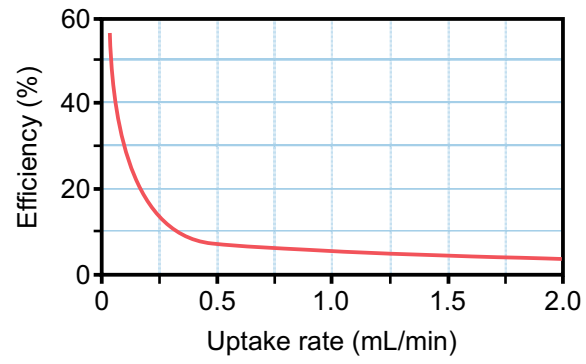
(A) Concentric nebulizer



(B) Crossflow nebulizer

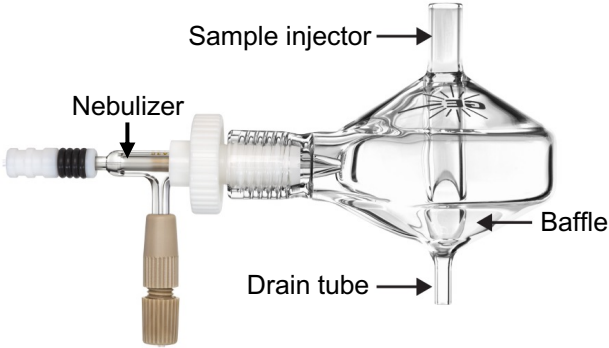


(C) Nebulizer transport efficiency



**Fig. 3**

(A) Cyclonic spray chamber



(B) Dual Scott/cyclonic spray chamber

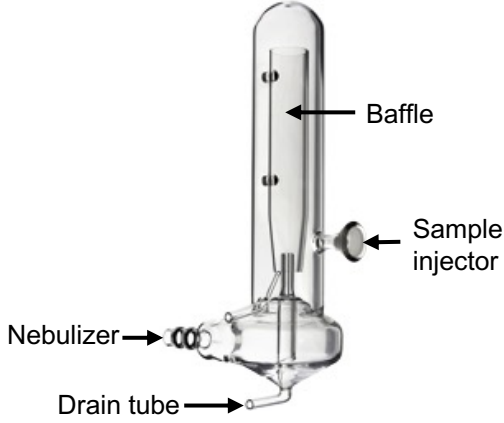
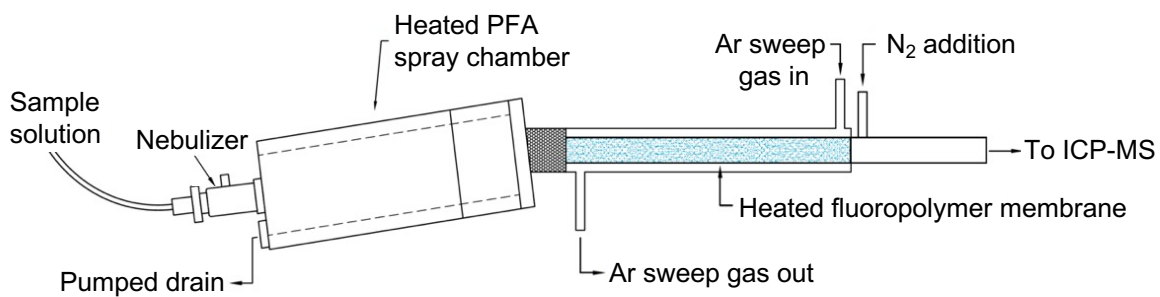


Fig. 4

(A) CETAC Aridus 3



(B) ESI Apex Omega

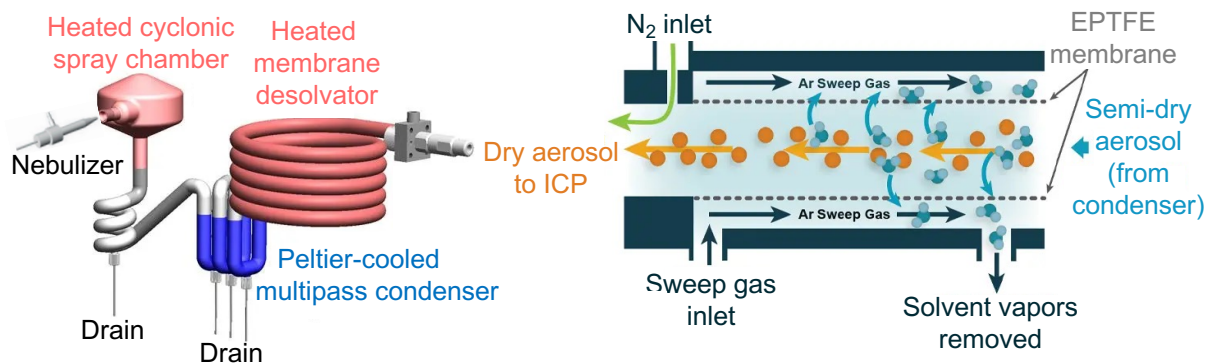
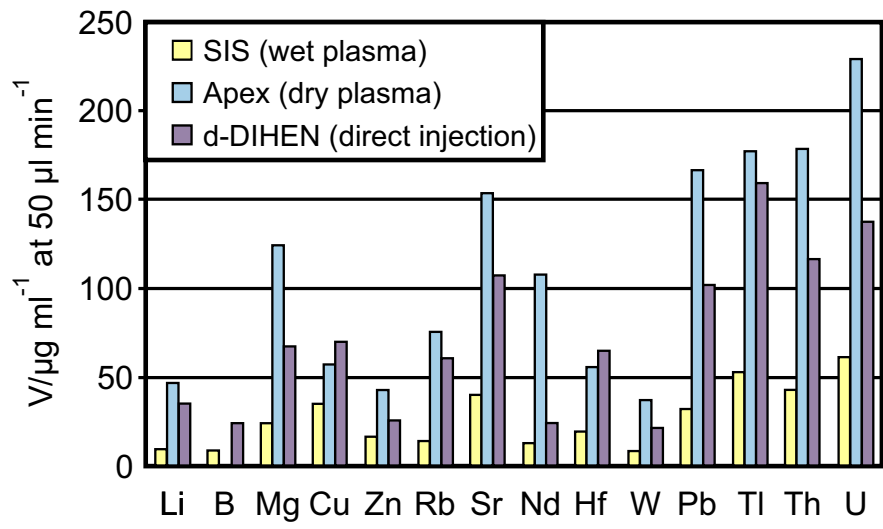
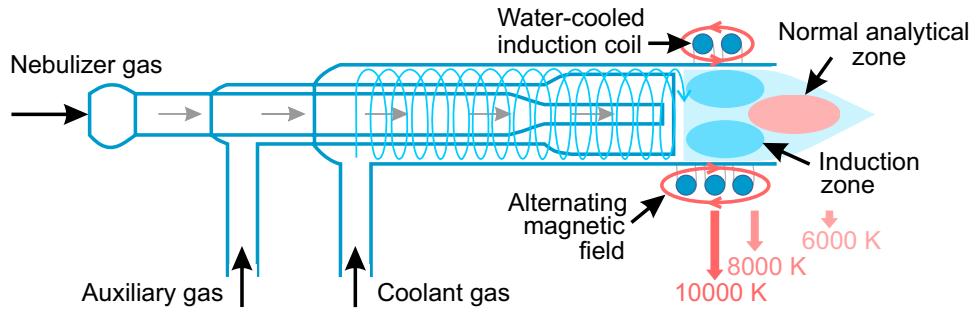


Fig. 5



**Fig. 6**

(a) Torch illustration



(b) Torch box configuration

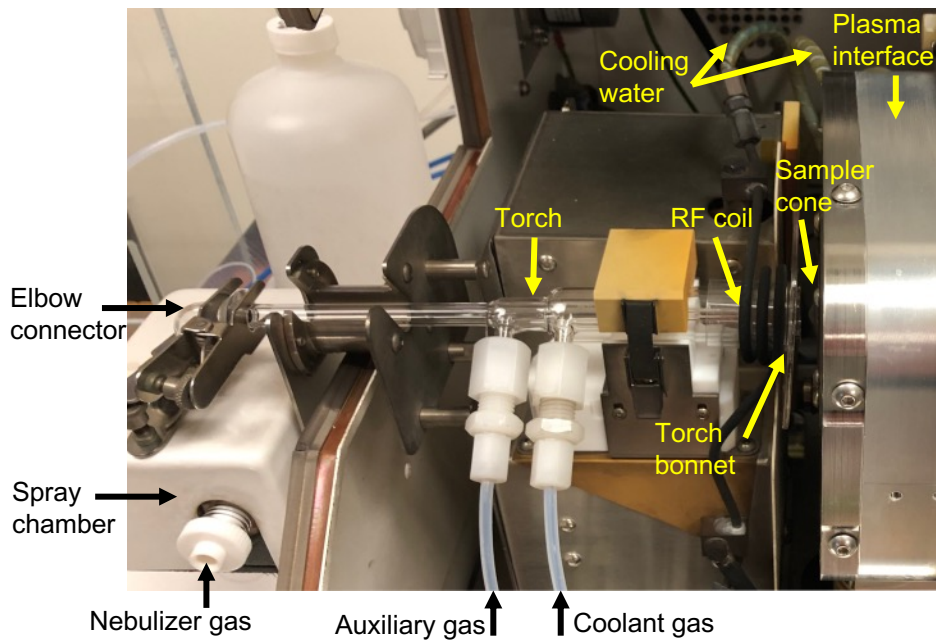
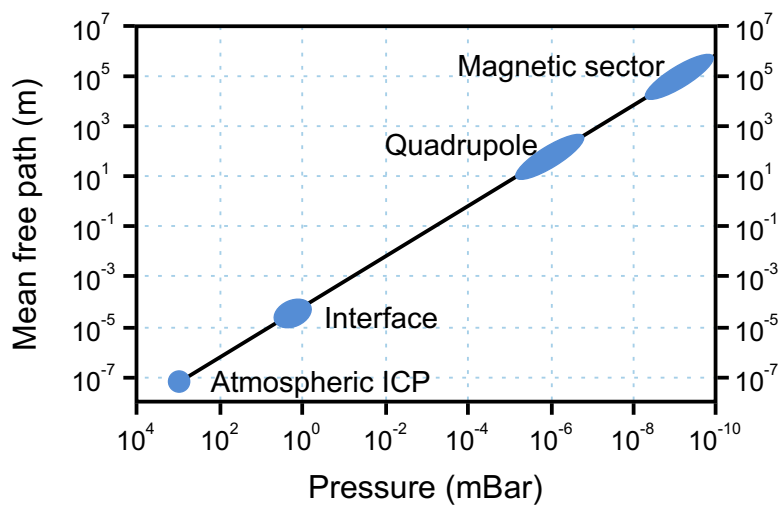


Fig. 7

(A) Pressure gradient across ICP-MS



(B) ICP-MS interface

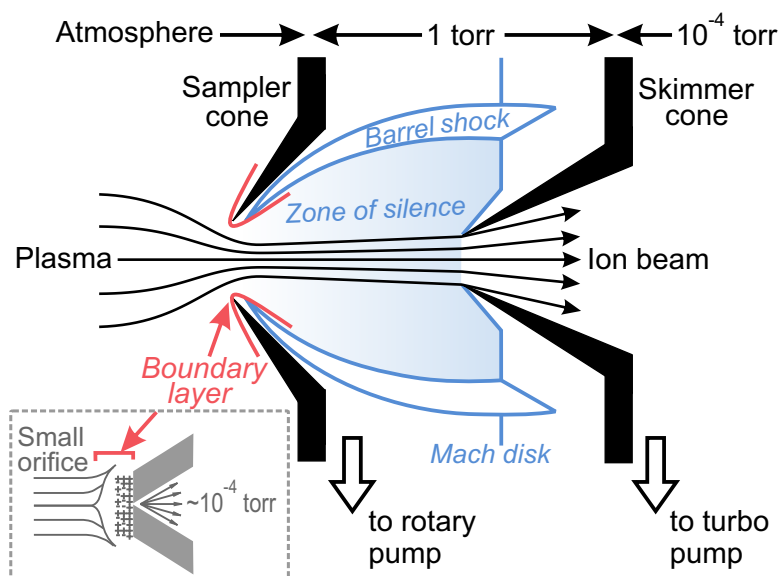
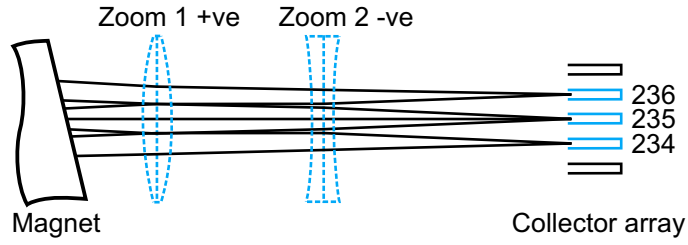
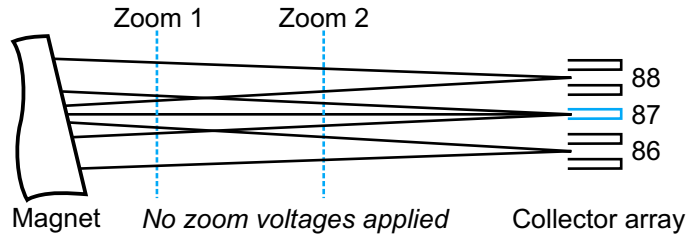


Fig. 8

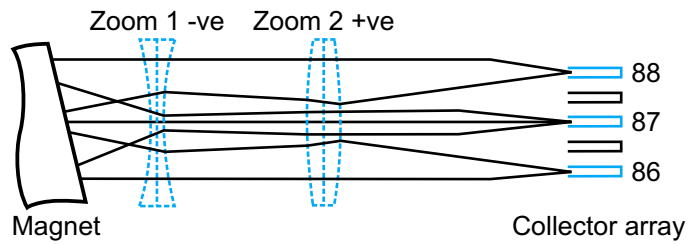
(A) Increased dispersion of U isotopes



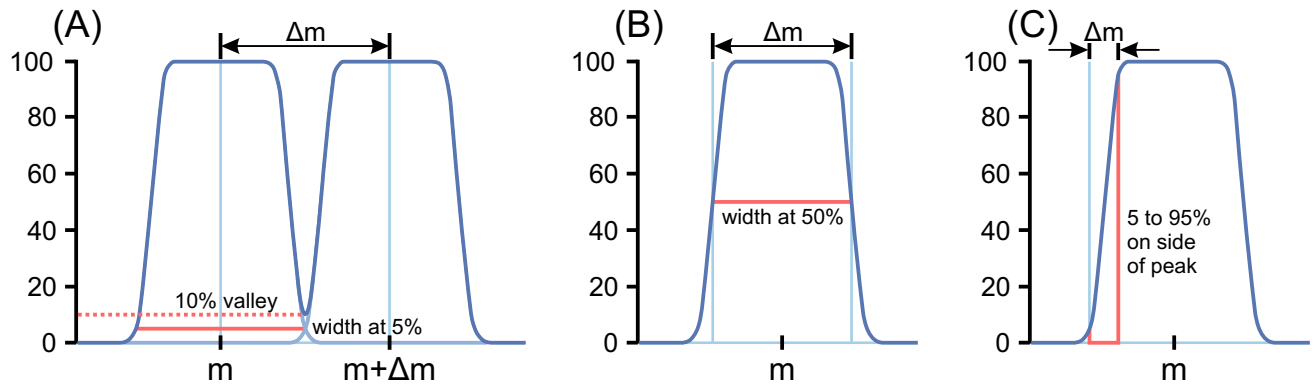
(B) Natural dispersion of Sr isotopes



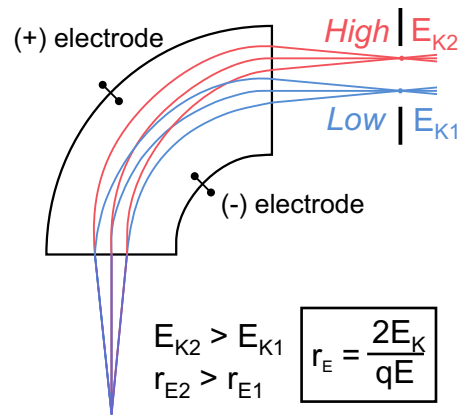
(C) Adjusted dispersion of Sr isotopes



**Fig. 9**



**Fig. 10**



**Fig. 11**

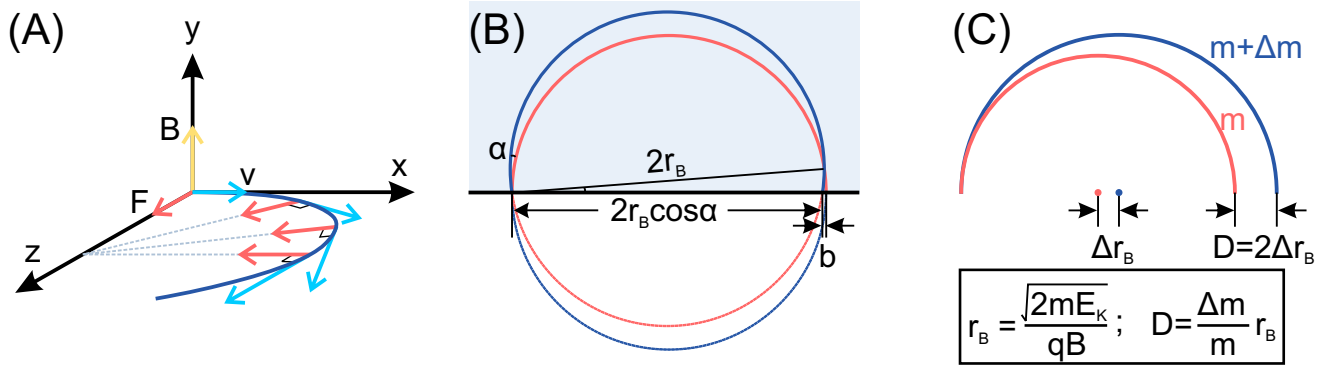
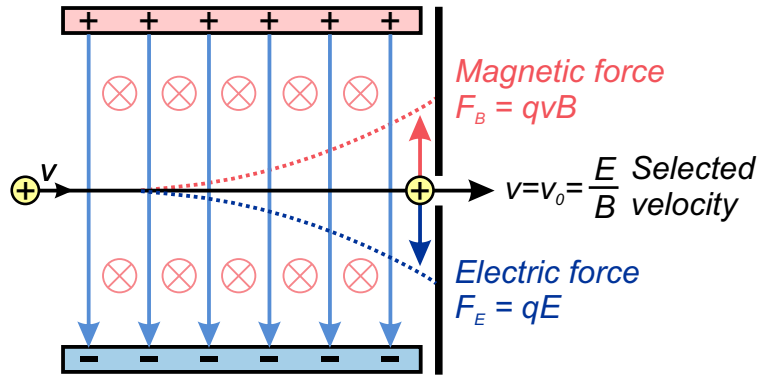
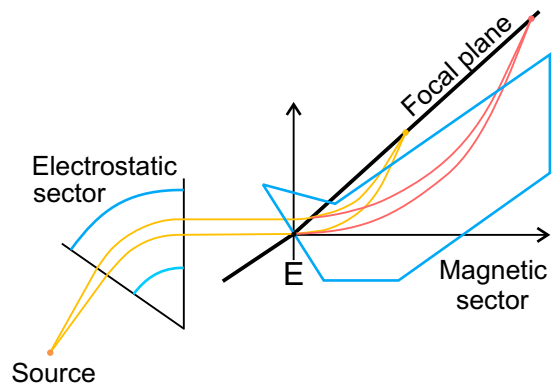


Fig. 12



**Fig. 13**

(A) Mattauch-Herzog geometry



(B) Forward Nier-Johnson geometry

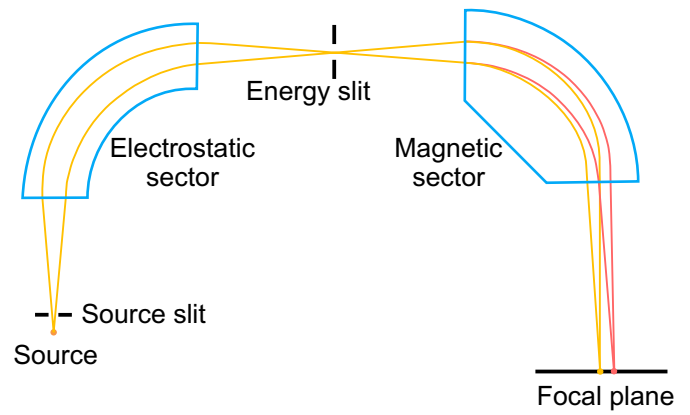
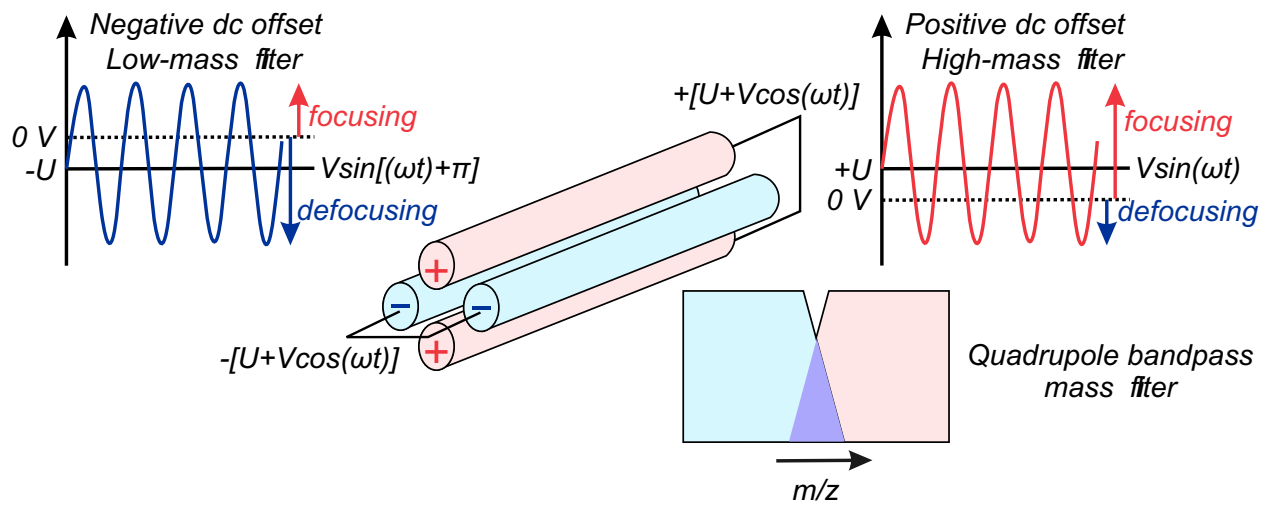
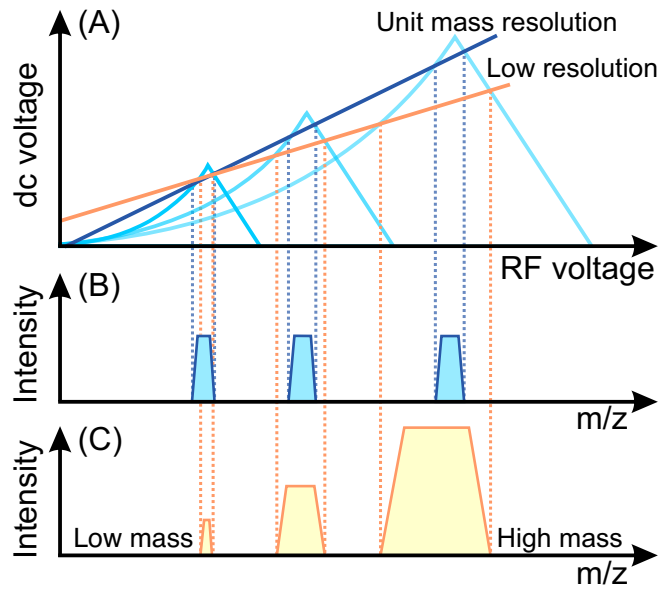


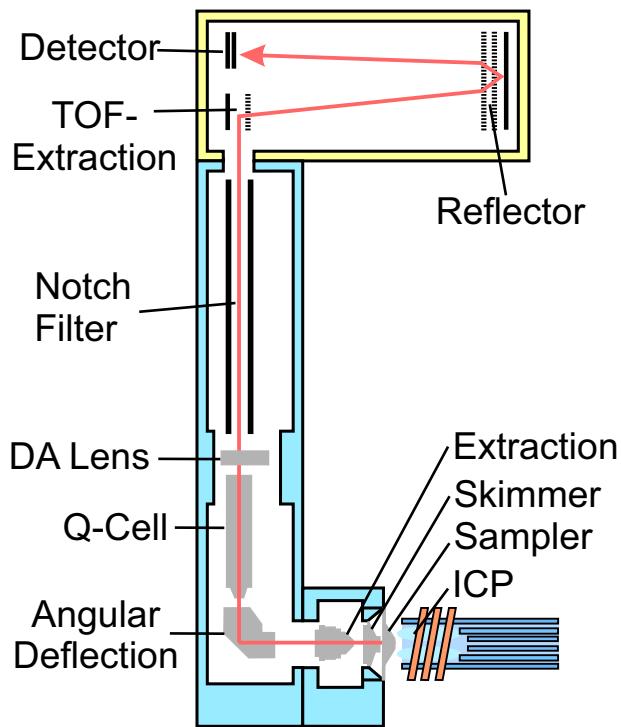
Fig. 14



**Fig. 15**



**Fig. 16**



**Fig. 17**

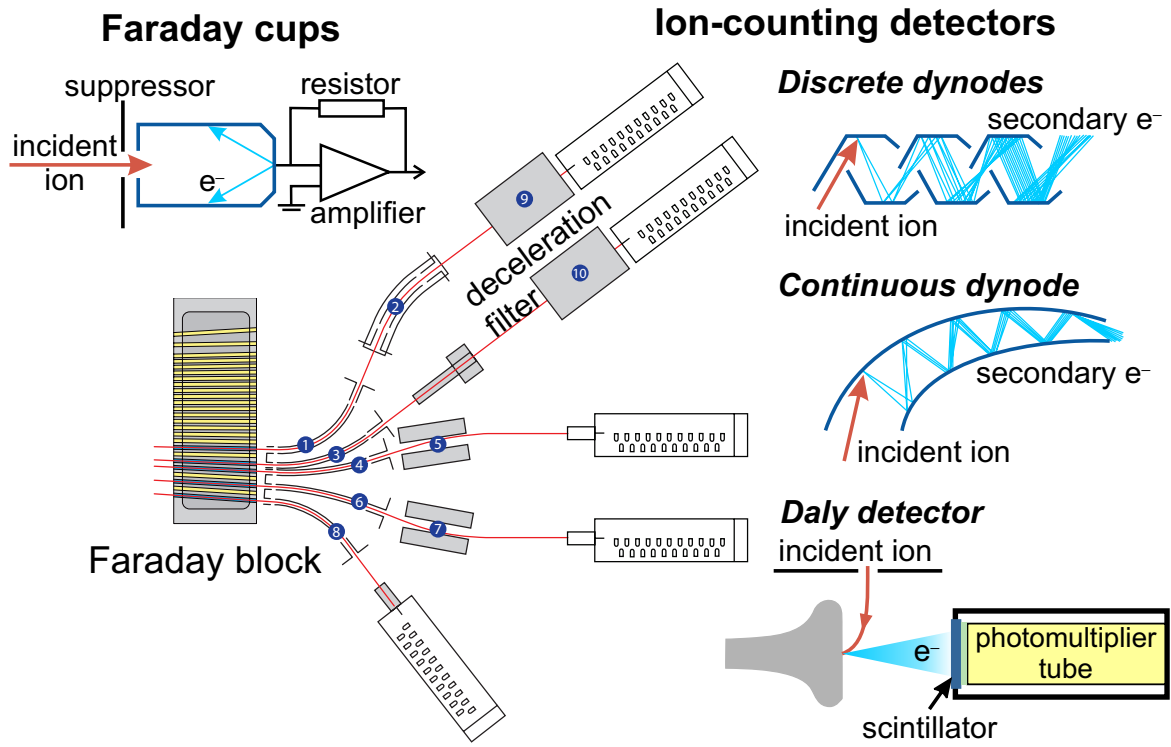
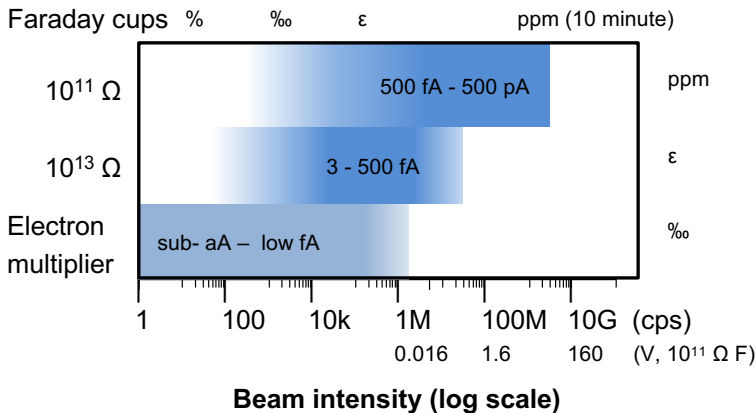
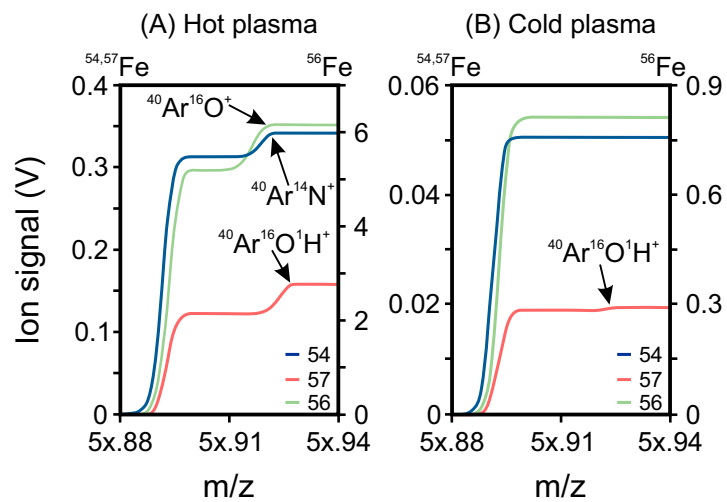


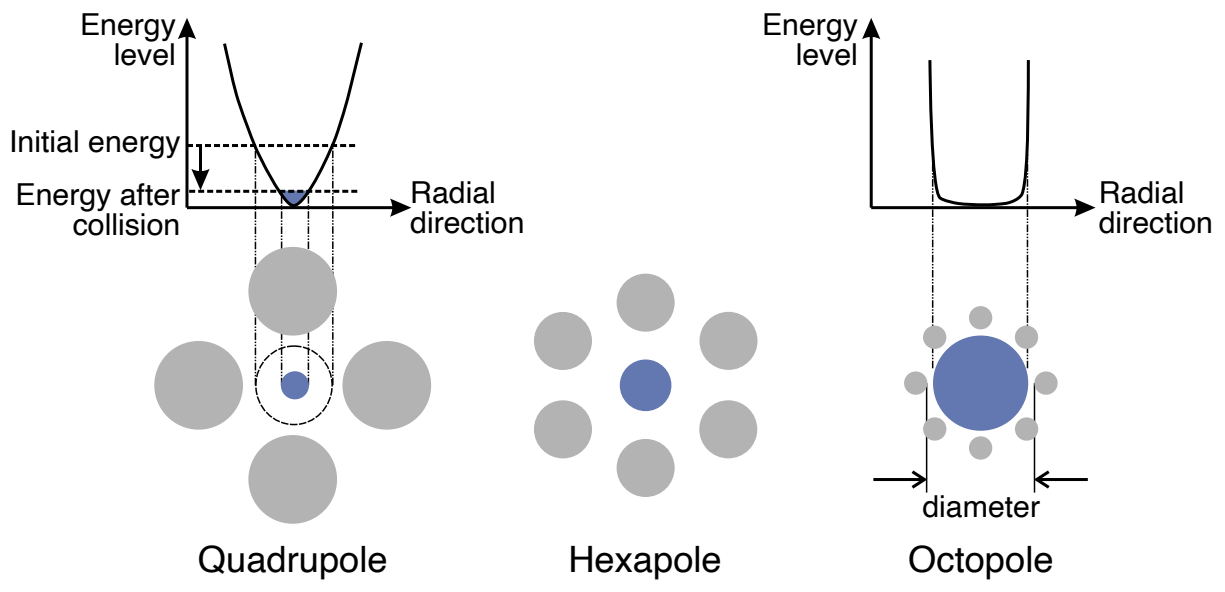
Fig. 18



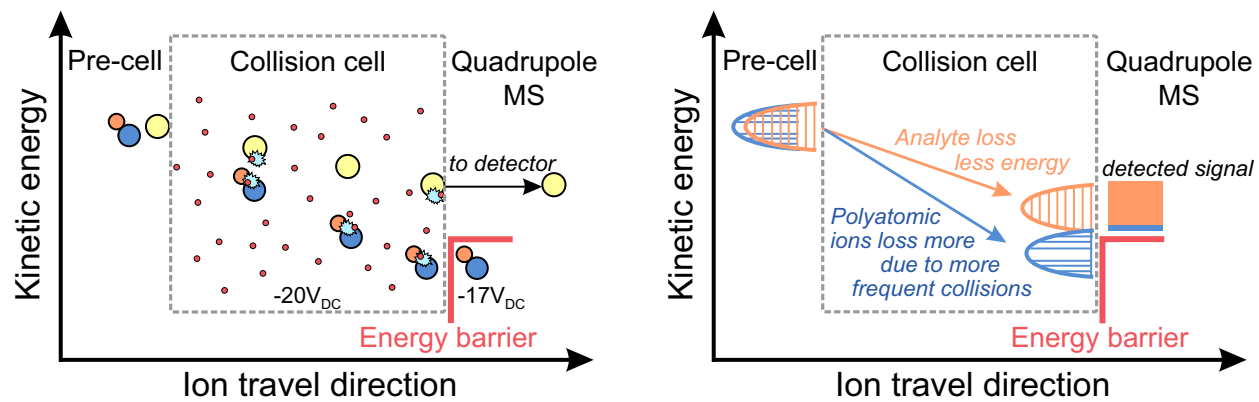
**Fig. 19**



**Fig. 20**

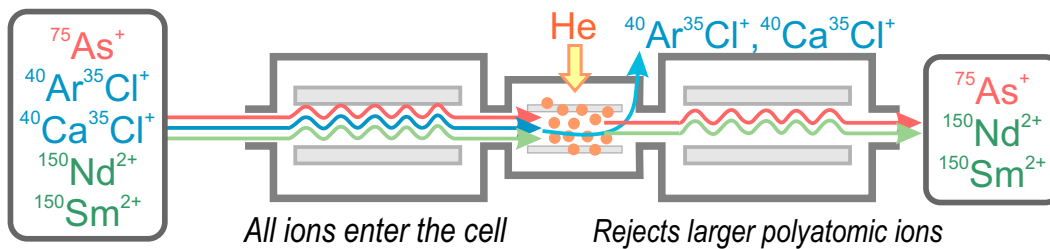


**Fig. 21**

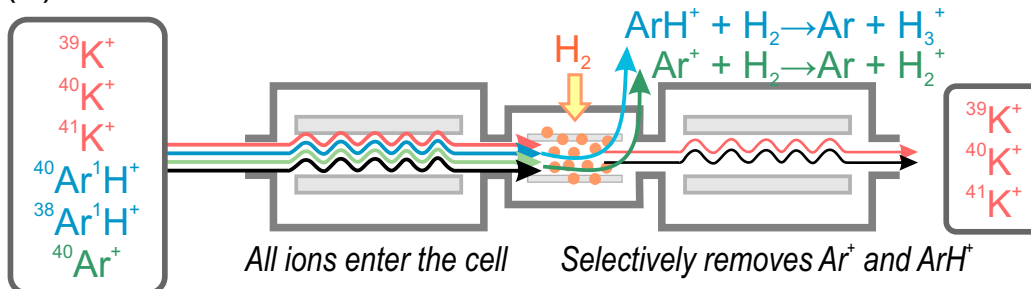


**Fig. 22**

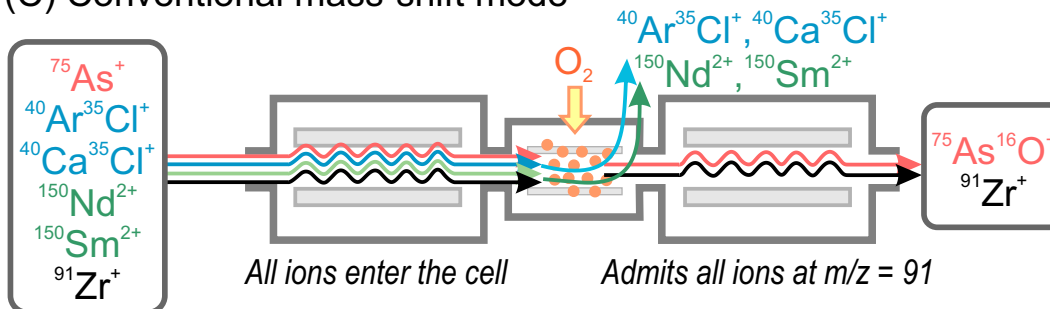
(A) Collision mode



(B) On-mass reaction mode



(C) Conventional mass-shift mode



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

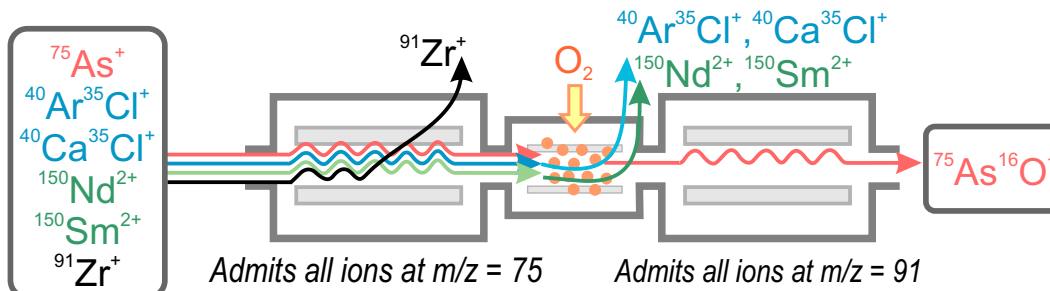


Fig. 23

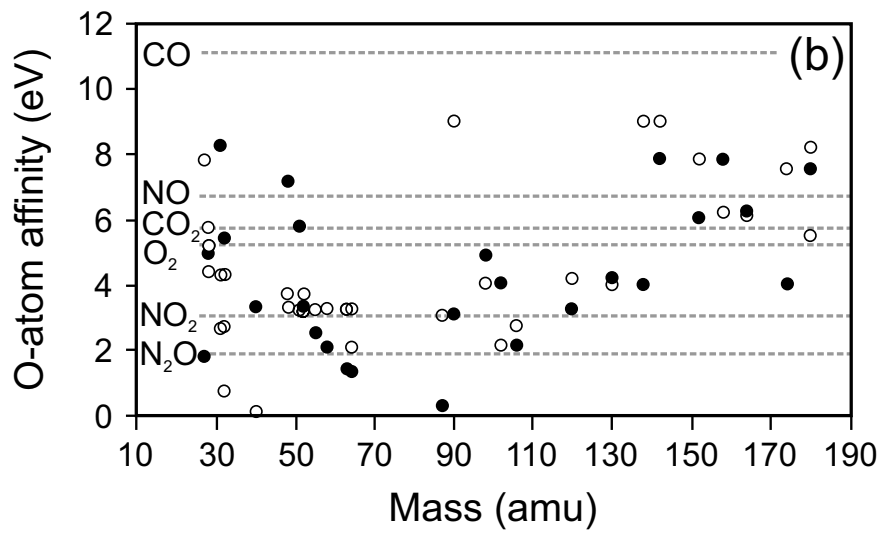
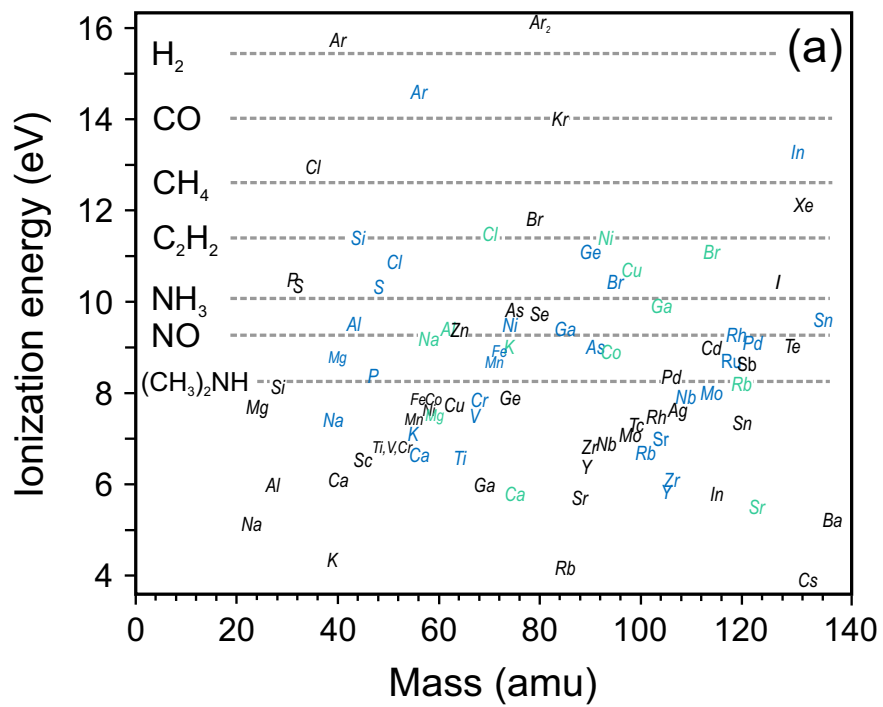
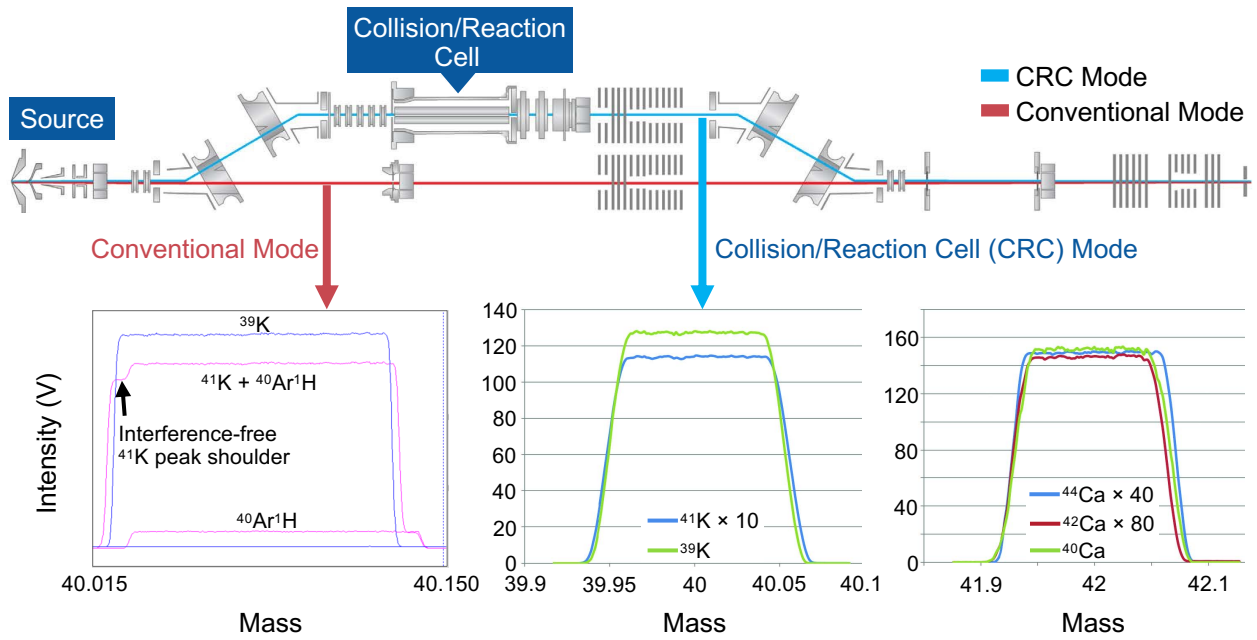
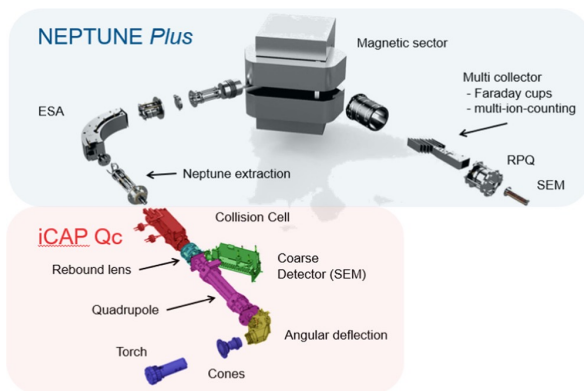


Fig. 24

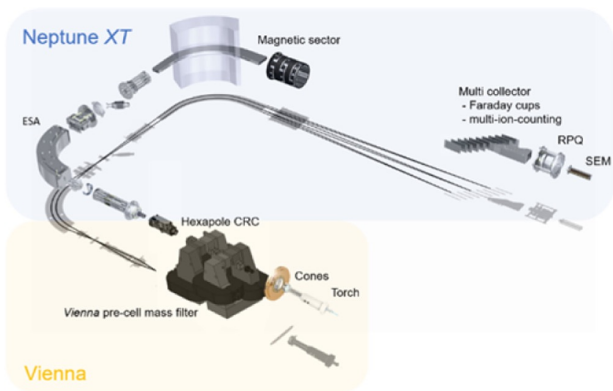


**Fig. 25**

(A) Prototype: Proteus



(B) Prototype: Vienna



(C) Neoma

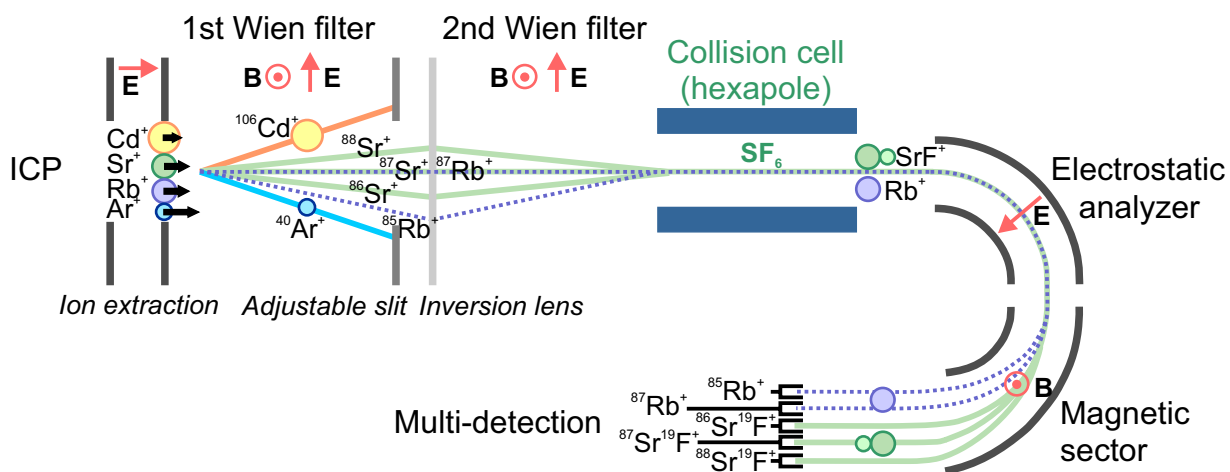
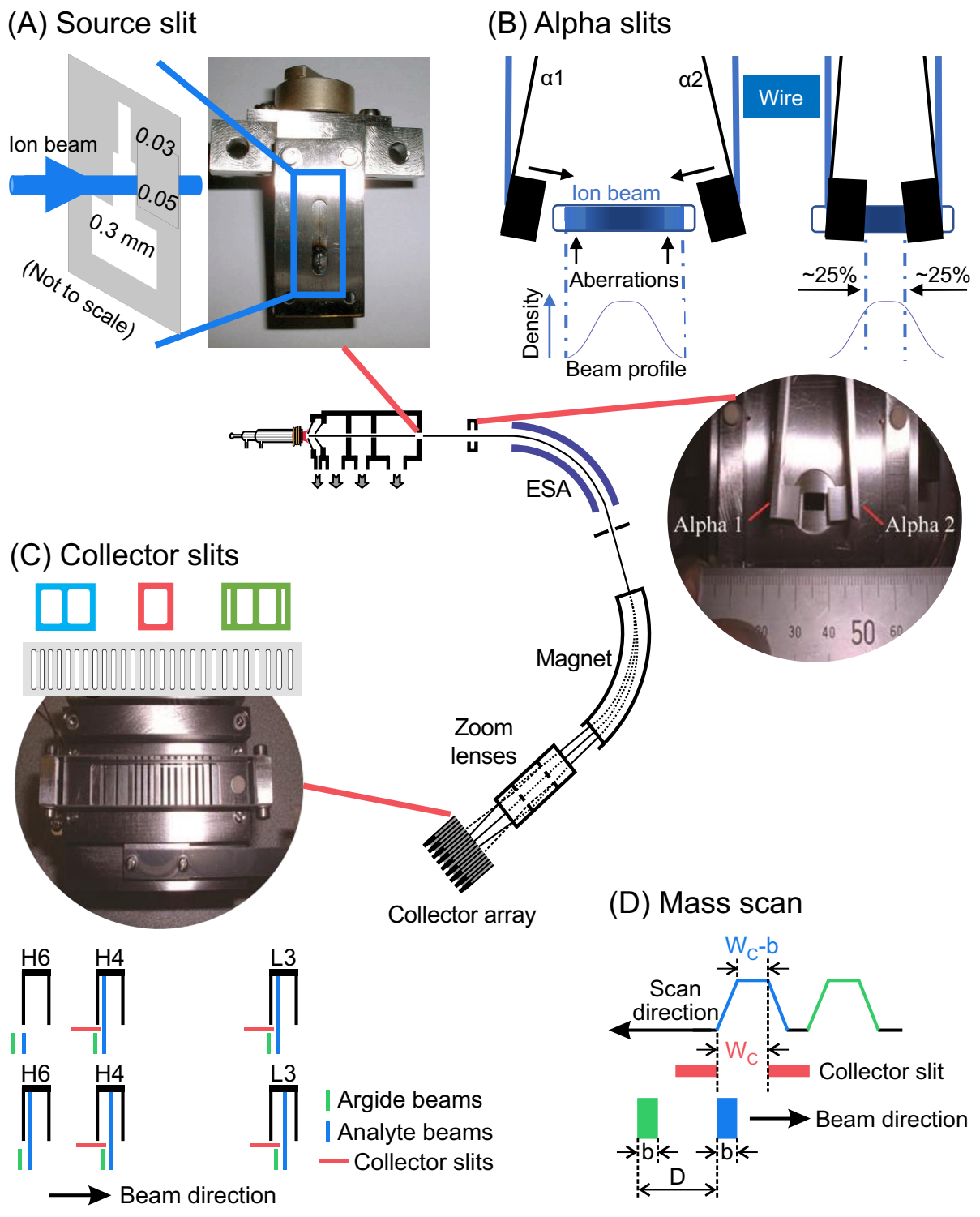
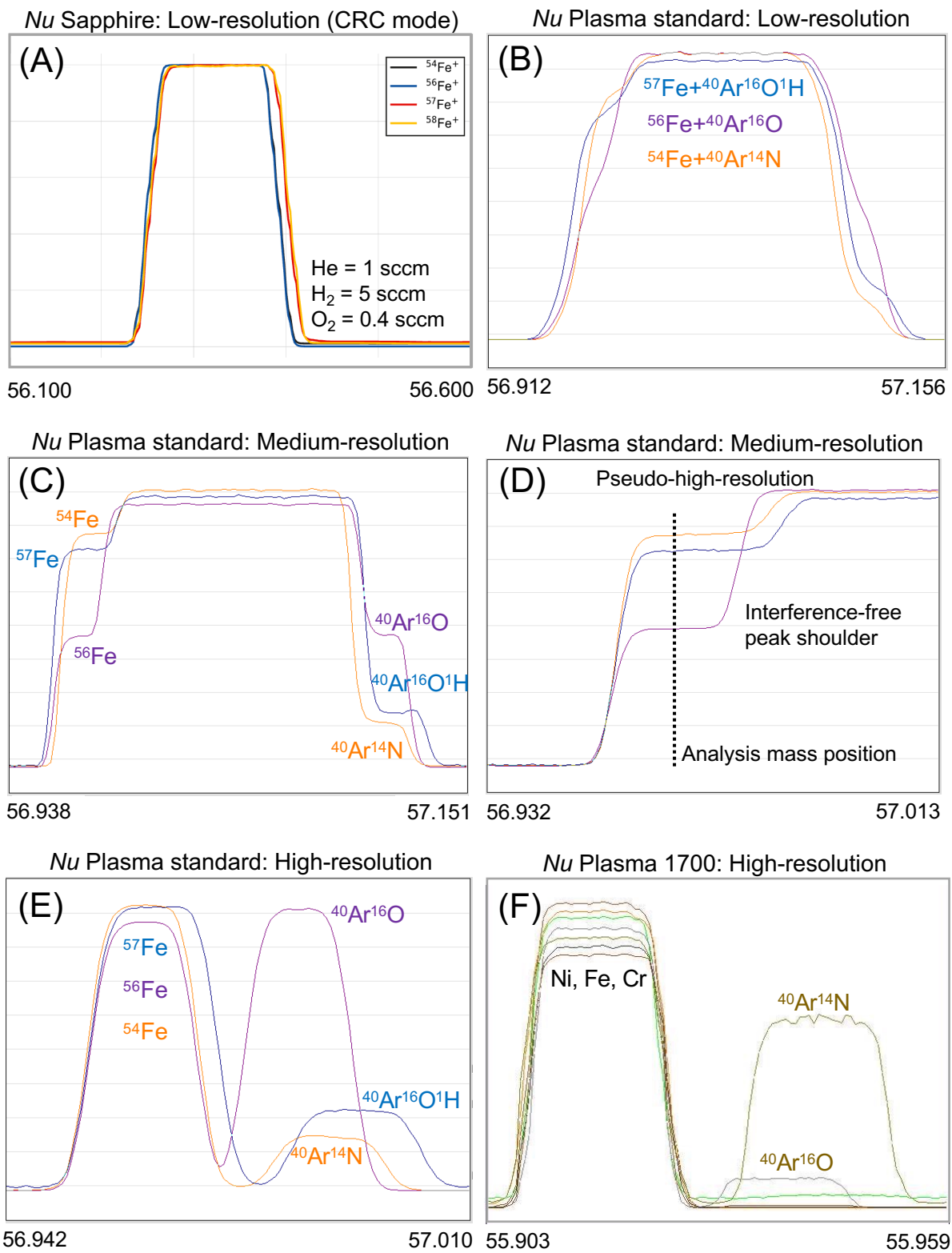


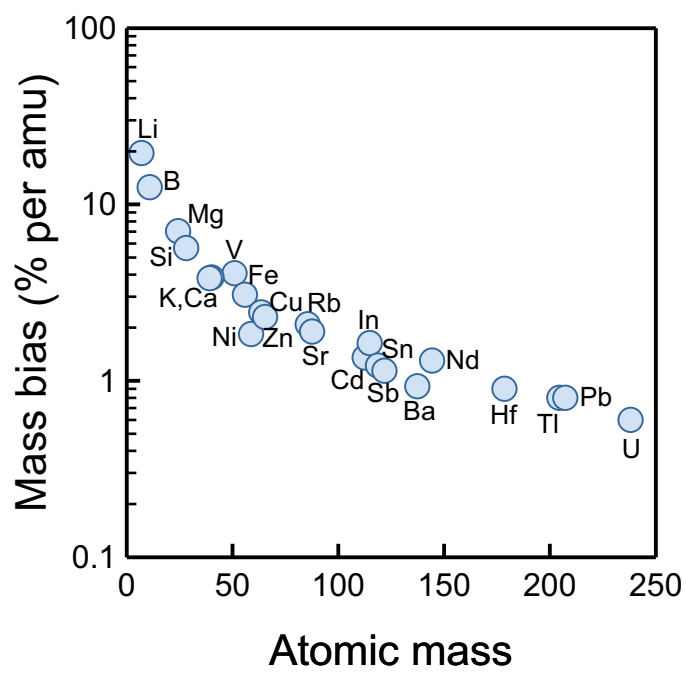
Fig. 26



**Fig. 27**



**Fig. 28**



**Fig. 29**