Review: Sulfur Analysis using Inductively Coupled Plasma Mass Spectrometry

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Received: *August 22, 2023;* ***Revised:*** *October 19, 2023;* ***Accepted:*** *October 22, 2023;* ***Available online:*** *October 22, 2023.*

DOI: 10.46770/AS.2023.187

ABSTRACT: This paper reviews the use of inductively coupled plasma mass spectrometry (ICP-MS) for sulfur analyses, covering articles published between January 2015 and April 2023. The ICP-MS instruments reported in the articles were classified as quadrupole ICP-MS, tandem quadrupole ICP-MS, high resolution ICP-MS, and multi-collector ICP-MS, each accounting for over 20% of the articles. Each type of ICP-MS instrument achieved detection limits < 1.0 ng/g. Laser ablation and chromatography hyphenated ICP-MS accounted for > 30% of the articles, with special attention paid to direct/imaging and speciation analyses. The leading research field in sulfur analysis is geology, followed by biology, environment, food/feed, and energy. Determination of sulfur concentrations, chemical speciation analysis of sulfur compounds, and sulfur isotope analysis accounted for approximately 30–40% of the articles. The most frequently measured sulfur isotope was ^{32}S, followed by ^{34}S and ^{33}S, whereas one article reported the measurement of ^{36}S. Selected topics of sulfur analysis using ICP-MS in research fields, hyphenated instruments, and typical applications are also introduced.

INTRODUCTION

Sulfur has four stable isotopes, namely, ^{32}S (94.99%), ^{33}S (0.75%), ^{34}S (4.25%), and ^{36}S (0.01%).[1] Sulfur is one of the major elements on Earth and attracts attention from various research fields including geochemistry (for example, sulfur-containing minerals such as sulfate, pyrite, and gypsum), biology (for example, sulfur-containing proteins, peptides, thiocyanate, xanthates, and amyloid-β), materials (for example, sulfur-containing nanoparticles), environmental sciences (for example, sulfur-related pollution), and other research fields.

Sulfur can be analyzed using multiple methods such as X-ray fluorescence spectrometry, titration, coulometry, combustion with thermal conductivity or infrared detection, inductively coupled plasma optical emission spectrometry, and inductively coupled plasma mass spectrometry (ICP-MS).[2]

Samples for ICP-MS analysis are introduced into argon plasma, where the sulfur content is ionized, and then extracted into the mass spectrometer system through a multiple-cone interface. Singly charged sulfur ions separate from other ions based on their mass-to-charge (m/z) ratio and are detected as electronic signals by a detector. Despite the relatively high first ionization energy of sulfur, the current ICP-MS technology is expected to achieve a detection limit for sulfur in the parts-per-billion range, which is superior to that of other methods by two to three orders of magnitude. Moreover, ICP-MS can be used for isotopic analysis, which cannot be accomplished using other methods.

In excess of ten articles per year focusing on ICP-MS for determining the sulfur concentration or sulfur isotope ratio by measuring stable sulfur isotopes have been published in recent years. In 2015, Martinez-Sierra *et al*. published a review on the application of ICP-MS for sulfur analysis emphasizing sulfur-specific (including peptides/proteins, pharmaceuticals/metallodrugs, and isotopic labeling) detection using hyphenated techniques (including liquid chromatography (LC), gas chromatography (GC), capillary electrophoresis (CE), and laser

ablation (LA)) and covering sulfur isotope ratio measurements.[3] Chahrour and Malone reviewed ICP-MS applications in quantitative proteomics and partly reviewed some sulfur-related studies published from 2015 to 2017.[4] Fuentes-Cervantes *et al*. recently reviewed the analysis of nanoparticle-protein coronas.[5]

This article reviews the application of ICP-MS for sulfur analysis, mainly focusing on articles published between 2015 and 2022 and some published in 2023. This review explores the ICP-MS models used for sulfur analysis, hyphenated instruments, strategies for spectral interference, detection limits, and typical applications. The author hopes that this review can provide valuable information for both beginners in ICP-MS who want to analyze sulfur and experts who have performed many studies on sulfur analysis using ICP-MS.

RESULTS AND DISCUSSION

Table 1 summarizes the articles covered in this review. Fig. 1 plots the number of articles published per year. Fig. 1 shows that between 2015 and 2022, except for 2017, at least 12 articles on the use of ICP-MS for sulfur analysis were published every year (that is, an average of one article per month). Such high-frequency publications indicate that the use of ICP-MS for the analysis of sulfur is a topic worthy of further study.

ICP-MS types and models used for sulfur analysis. As summarized in Table 1,[6–113] the ICP-MS instruments used for sulfur analysis can be classified as quadrupole ICP-MS (ICP-QMS), tandem quadrupole ICP-MS with a reaction cell (ICP-QMS/QMS), high-resolution ICP-MS (HR-ICP-MS), and multi-collector ICP-MS (MC-ICP-MS).

Notably, the original equipment manufacturers of ICP-QMS/QMS equipment use different names for their products, such as ICP-QQQ, triple-quadrupole ICP-MS, and multi-quadrupole ICP-MS. ICP-QMS/QMS is used in this review to clarify the presence of two quadrupoles capable of selecting an ion based on its *m*/*z*. HR-ICP-MS is also known as sector field ICP-MS. HR-ICP-MS was reviewed in this article because of its capability for medium resolution (MR) and high resolution (HR) measurements.

Figure 2 (A) plots the distribution of the ICP-MS types used for sulfur analyses. Each type of ICP-MS accounts for at least 20% of the sulfur analysis applications. Notably, ICP-QMS/QMS has been commercially available since the early 2010s, three decades after the availability of the other three types of ICP-MS. The 30% share of ICP-QMS/QMS applications (number of articles for ICP-QMS/QMS (32) divided by the total number of articles (118)) in sulfur analysis using ICP-MS may be due to its effectiveness in separating spectral interferences without a trade-off in sensitivity. ICP-QMS (including that without a collision/reaction cell) has also been widely used for sulfur analysis, which can be attributed to its accessibility in many laboratories and robustness to high-matrix samples. The share of HR-ICP-MS can be attributed to the fact that it provides a simple solution for separating spectral interference and an appreciably low detection limit for sulfur analysis. The share of MC-ICP-MS can be attributed to its excellent precision in isotope analyses, where the simultaneous detection of multiple isotopes results in a stable isotope ratio independent of the innate fluctuation of the argon plasma.

Fig. 1 Number of articles on sulfur analysis using ICP-MS published every year from 2015 to 2023. (Green, less than 10 articles per year; Yellow, over 10 articles per year.)

Fig. 2 Types and manufacturers of ICP-MS used for sulfur analysis. (A) Type of ICP-MS and number (percentage) of articles and (B) ICP-MS manufacturers and number (percentage) of articles.

Table 2 summarizes the main manufacturers of ICP-MS equipment and their models used in sulfur analysis, and the share of their applications (listed in Table 1) in sulfur analysis is plotted in Fig. 2 (B). Figure 2 (B) shows that the share fractions of the Thermo Fisher Scientific, Agilent Technologies, Nu Instrument, and PerkinElmer ICP-MS models are 47, 40, 16, and 9%, respectively. Thermo Fisher Scientific has the largest share of reports, which can be attributed to its products, which cover the entire list of the four types of ICP-MS. Agilent Technologies has the second-largest share of reports, which can be attributed to its

Table 1. Articles reviewed in this study

Year published	ICP-MS instrument		Hyphenated Instrument [b]	Matrix of sample	Strategy for spectral interference	Measurand	Measured isotope	Reference No.
	Type [a]	Model						
2015	ICP-QMS/QMS	Agilent 8800	AF4	Quantum dot	Mass-shift	Speciation	^{32}S	6
2015	ICP-QMS/QMS	Agilent 8800	SEC	Protein	Mass-shift	Speciation	^{32}S, ^{34}S	7
2015	MC-ICP-MS	Nu Plasma HR	LA	Sulfate, sulfide	Pseudo MR, Pseudo HR	Isotope	^{32}S, ^{33}S, ^{34}S	8
2015	HR-ICP-MS	Element 2	LA	Human serum	MR (4000)	Concentration	^{32}S, ^{34}S	9
2015	ICP-QMS/QMS	Agilent 8800	GC	Food sample	Mass-shift	Speciation	^{32}S	10
2015	MC-ICP-MS	Neptune Plus	Not available	Sediment pore water	MR (ca. 3000)	Isotope, Concentration	^{32}S, ^{33}S, ^{34}S	11
2015	ICP-QMS	NexION 300D	LC	Dry vegetables and fruits	O_2 reaction	Speciation	^{32}S	12
2015	ICP-QMS/QMS	Agilent 8800	HPLC	Synthetic DNA-protein	Mass-shift	Speciation	^{32}S	13
2015	ICP-QMS, HR-ICP-MS	Agilent 7700x, Element 2	UPLC	Phosphorothioate oligonucleotides	He collision for ICP-QMS, MR (4000) for HR-ICP-MS	Speciation	^{32}S	14
2015	ICP-QMS/QMS	Agilent 8800	Not available	Wine	Mass-shift	Concentration	^{32}S, ^{34}S	15
2015	MC-ICP-MS, HR-ICP-MS	Neptune plus, Element 2	HPLC, desolvation device	Mice urine	Pseudo HR for MC-ICP-MS, MR for HR-ICP-MS	Speciation	^{32}S, ^{33}S, ^{34}S	16
2015	ICP-QMS, HR-ICP-MS	NexION 300S, Element 2	HPLC	Phosphopeptides	O_2 reaction for ICP-QMS, MR (4000) for HR-ICP-MS	Speciation	^{32}S, ^{33}S, ^{34}S	17
2016	Not available	Not available	CE	Protein, Au nanoparticle	Not available	Speciation	^{34}S	18
2016	MC-ICP-MS, ICP-QMS	Neptune plus, iCAP-Q	LA	Sulfide	MR	Isotope, Concentration	^{32}S, ^{33}S, ^{34}S	19
2016	MC-ICP-MS	Nu Plasma HR	LA	Sulfide	HR (10000 for ^{34}S, 12000 for ^{32}S)	Isotope	^{32}S, ^{34}S	20
2016	MC-ICP-MS, HR-ICP-MS	Neptune plus, Element 2	HPLC	Methionine in human blood plasma	Pseudo MR for MC-ICP-MS, MR (4000) for HR-ICP-MS	Speciation	^{32}S, ^{33}S, ^{34}S	21
2016	HR-ICP-MS	Element XR	Microwave induced combustion	Coal	MR (>4500)	Concentration	^{32}S, ^{33}S, ^{34}S	22
2016	ICP-QMS	ELAN 6100 DRC II	LA	Pea seedlings	Not available	Concentration	^{34}S	23
2016	MC-ICP-MS	Neptune Plus	Desolvation device	Bovine serum, human serum and plasma	HR (〜9000)	Isotope	^{32}S, ^{33}S, ^{34}S	24
2016	MC-ICP-MS	Neptune plus	Desolvation device	Model solution	MR (3000)	Isotope	^{32}S, ^{33}S, ^{34}S	25
2016	HR-ICP-MS	Element 2	Not available	Sediments	MR (4000)	Concentration	^{32}S	26
2016	MC-ICP-MS	Neptune plus	LA	Sulfides, elemental sulfur	MR (〜4000)	Isotope	^{32}S, ^{33}S, ^{34}S	27
2016	ICP-QMS	X series 2	Not available	Natural rubber	O_2 reaction	Concentration	^{32}S	28
2016	MC-ICP-MS, HR-ICP-MS	Nu Plasma HR, Element XR	Not available	Environmental aqueous sample	MR (2300) for MC-ICP-MS, MR (4000) for HR-ICP-MS	Isotope, Concentration	^{32}S, ^{33}S, ^{34}S	29
2016	ICP-QMS, HR-ICP-MS, MC-ICP-MS, ICP-QMS/QMS	NexION 300D, Agilent 7700, Agilent 8800, Element 2, Nu Plasma HR	Desolvation device	Reference materials	MR for HR-ICP-MS and MC-ICP-MS, reaction/collision for ICP-QMS, mass-shift for ICP-QMS/QMS	Isotope	^{32}S, ^{34}S	30

Year published	ICP-MS instrument		Hyphenated Instrument [b]	Matrix of sample	Strategy for spectral interference	Measurand	Measured isotope	Reference No.
	Type [a]	Model						
2016	ICP-QMS, ICP-QMS/QMS	ELAN DRC-e, Agilent 8800	HPLC, desolvation, device	Peptides in human plasma	O_2 reaction for ICP-QMS, mass-shift for ICP-QMS/QMS	Speciation	^{32}S, ^{34}S	31
2017	MC-ICP-MS	Neptune Plus	LA	Ag_2S, elemental S, chalcopyrite, sphalerite, pyrite, synthetic sulfide	N_2 mixing plasma, MR (～4000)	Isotope	^{32}S, ^{33}S, ^{34}S	32
2017	MC-ICP-MS	Nu Plasma 1700	LA	Pyrite, chalcopyrite, sphalerite, and ganela	MR (RP 10000) and HR (RP18000)	Isotope	^{32}S, ^{33}S, ^{34}S	33
2017	MC-ICP-MS	Neptune	Desolvation device	Silver sulfides, seawater, Archean sulfide, pore fluids	MR (5000), background correction, desolvation	Isotope	^{32}S, ^{33}S, ^{34}S	34
2017	ICP-QMS	iCAP-Qc	LA	Pyrite	Not available	Concentration	Not available	35
2017	ICP-QMS	NexION 300D	Not available	Biodiesel	O_2 reaction	Concentration	^{32}S	36
2017	HR-ICP-MS	Element XR	LA	Fluid inclusion	MR (4000)	Concentration,	^{34}S	37
2017	MC-ICP-MS, ICP-QMS	Neptune Plus, Agilent 7700s	LA	Pyrite	MR (ca. 3200) for MC-ICP-MS, not available for ICP-QMS	Isotope, Concentration	^{32}S, ^{33}S, ^{34}S	38
2017	MC-ICP-MS	Nu plasma 1700	LA	Sulfide	MR (RP, 10000)	Isotope	^{32}S, ^{33}S, ^{34}S	39
2018	HR-ICP-MS	Element XR	GPC	Petroleum products	MR (4000)	Speciation	^{32}S	40
2018	MC-ICP-MS	Neptune Plus	LA	Sulfide	N_2 addition plasma, MR (ca. 4000)	Isotope	^{32}S, ^{33}S, ^{34}S	41
2018	MC-ICP-MS	Neptune Plus	LA	Ore fluid	Not available	Isotope	^{32}S, ^{33}S, ^{34}S	42
2018	ICP-QMS	ELAN DRC-e	LA	Magmatic-hydrothermal fluid	Dry plasma	Concentration	^{32}S	43
2018	HR-ICP-MS	Element XR, Element 2	LA	Copper metal	MR (4000)	Concentration	^{32}S, ^{34}S	44
2018	ICP-QMS	Not available	Not available	Wastewater	H_2 and He reaction	Concentration	^{34}S	45
2018	MC-ICP-MS	Neptune Plus	Not available	Sulfur-bearing minerals	HR	Isotope	^{32}S, ^{33}S, ^{34}S	46
2018	ICP-QMS/QMS	Agilent 8800	Not available	Model solution	Mass shift	Concentration	^{32}S	47
2018	ICP-QMS	Agilent 7500x	Not available	Gypsum	Signal suppression (omega-bias) and concentration-gradient-method	Isotope	^{32}S, ^{34}S	48
2018	MC-ICP-MS	Nu Plasma 1700	LA	Sulfide	MR (2500 for $^{32,34}S$, 5000 for ^{33}S)	Isotope	^{32}S, ^{33}S, ^{34}S	49
2018	ICP-QMS/QMS	Agilent 8800	Not available	Model cell	Mass shift	Concentration	^{32}S	50
2018	MC-ICP-MS	Nu Plasma II	IC	Thioarsenates	HR (～7000)	Isotope	^{32}S, ^{33}S, ^{34}S	51
2019	Not available	Not available	LA	Sulfide	Not available	Isotope	Not available	52
2019	HR-ICP-MS, MC-ICP-MS	Element XR, Neptune Plus	Not available	Natural water	MR, (HR-ICP-MS, >2500; MC-ICP-MS, 3500)	Concentration, Isotope	^{32}S, ^{33}S, ^{34}S	53
2019	ICP-QMS	NexION 300D	Not available	Human serum, blood plasma and whole blood	O_2 reaction	Concentration	^{32}S	54
2019	ICP-QMS	ELAN 6100 DRC II	IC	Dry food	O_2 reaction	Speciation	^{32}S, ^{34}S	55
2019	ICP-QMS	iCAP RQ	SEC	Immunochemical assays	O_2 reaction	Speciation	^{32}S, ^{34}S	56
2019	ICP-QMS/QMS	Agilent 8800	GC	Gasoline	Mass shift	Speciation	^{32}S	57

Year published	ICP-MS instrument		Hyphenated Instrument [b]	Matrix of sample	Strategy for spectral interference	Measurand	Measured isotope	Reference No.
	Type [a]	Model						
2019	MC-ICP-MS	Nu Plasma 1700	LA	Zircon	MR (2500 for ^{32,34}S, 5000 for ^{33}S)	Isotope	^{32}S, ^{33}S, ^{34}S	58
2019	ICP-QMS/QMS, HR-ICP-MS	Agilent 8800, Element XR	GPC (HR-ICP-MS)	Petroleum products	Mass shift for ICP-QMS/QMS, MR (4000) for HR-ICP-MS	Speciation	^{32}S, ^{34}S	59
2019	ICP-QMS/QMS	Agilent 8800	CE	Liposomal, sulfate	Mass shift	Speciation	^{32}S	60
2019	ICP-QMS	iCAP-Q	Not available	Feed	Kinetic energy discrimination	Concentration	^{34}S	61
2019	ICP-QMS/QMS	Agilent 8800	AF4	Nanoparticle-antibody	Mass shift	Speciation	^{32}S	62
2019	HR-ICP-MS	Element 2	Not available	Petroleum products	MR (4000)	Concentration	^{32}S, ^{34}S	63
2019	ICP-QMS/QMS	Agilent 8800	UPLC	Human plasma	Mass shift	Speciation	^{32}S, ^{34}S	64
2019	ICP-QMS	Agilent 7700x	Not available	Seaweed	He collision	Not available	Not available	65
2019	ICP-QMS	Elan DRC-e	LA	Glass, mineral, melt inclusion	Dry plasma	Concentration	^{32}S	66
2020	HR-ICP-MS	Element 2	Not available	Human serum, Au-nanoparticle	High resolution	Concentration	^{32}S	67
2020	MC-ICP-MS	Nu plasma II	LA	Sulfate	N_2 mix to Plasma	Isotope	^{32}S, ^{33}S, ^{34}S	68
2020	HR-ICP-MS	Element XR?	HPLC	Amyloid-beta (Aβ)	MR (4000)	Speciation	^{32}S, ^{34}S	69
2020	HR-ICP-MS	Element 2	Not available	Human serum, Fe-nanoparticle	MR	Concentration	^{32}S	70
2020	ICP-QMS/QMS	Agilent 8900	Not available	Standard solution	Mass shift	Isotope	^{32}S, ^{33}S, ^{34}S	71
2020	ICP-QMS/QMS	Agilent 8900	Not available	Single cell	Mass shift	Concentration	^{32}S	72
2020	HR-ICP-MS	Element XR	LC	Asphaltene	MR (4000)	Speciation	^{32}S	73
2020	ICP-QMS	Agilent 7700	LA	Black shale	Not available	Concentration	^{34}S	74
2020	ICP-QMS/QMS	Agilent 8800	Not available	Oligonucleotides	Mass shift	Concentration	^{32}S, ^{34}S	75
2020	ICP-QMS/QMS	iCap TQ	Not available	Uranium ore	Mass shift	Concentration	^{32}S	76
2020	ICP-QMS/QMS	Agilent 8800	LC	Petroleum products	Mass shift	Speciation	^{32}S	77
2020	ICP-QMS/QMS	Agilent 8800	Not available	Particulate matter	Mass shift	Concentration	^{32}S	78
2021	ICP-QMS	iCAP-Q	Not available	Water	O reaction	Concentration	^{32}S	79
2021	MC-ICP-MS	Nu Plasma II	LA	Magnetite, pyrite and pyrrhotite	N_2 mix to Plasma, MR (5000)	Isotope	^{32}S, ^{33}S, ^{34}S	80
2021	ICP-QMS/QMS	Agilent 8900	Not available	Dissolved organic matter	Mass shift	Concentration	^{32}S	81
2021	ICP-QMS/QMS	Agilent 8800	HPLC	Cultured mammalian cells	Mass shift	Speciation	^{32}S, ^{34}S	82
2021	ICP-QMS/QMS	Agilent 8900	Not available	Natural water	Mass shift	Isotope	^{32}S, ^{34}S	83
2021	ICP-QMS; MC-ICP-MS	Agilent 7700/7900; Neptune Plus	LA	Pyrite, chalcopyrite, sphalerite	Not available	Concentration; Isotope	^{32}S, ^{33}S, ^{34}S	84
2021	HR-ICP-MS	Element XR	LA	Copper and copper alloys	MR (>4300)	Concentration	^{32}S, ^{34}S	85
2021	ICP-QMS/QMS	Agilent 8800	LC	Human plasma	Mass shift	Speciation	^{32}S, ^{34}S	86

Year published	ICP-MS instrument		Hyphenated Instrument [b]	Matrix of sample	Strategy for spectral interference	Measurand	Measured isotope	Reference No.
	Type [a]	Model						
2021	HR-ICP-MS	Element 2	Not available	Iron oxide magnetic nanoparticles with protein	MR	Concentration	^{32}S	87
2021	MC-ICP-MS	Nu Plasma 1700	LA	Chalcopyrite	MR (2500)	Isotope	^{32}S, ^{33}S, ^{34}S	88
2021	ICP-QMS/QMS	Agilent 8800	Not available	Salmon SRM	Mass shift	Isotope	^{32}S, ^{33}S, ^{34}S	89
2021	ICP-QMS	iCAP-Q	LA	Human skin	Not available	Concentration	^{34}S	90
2021	ICP-QMS	Agilent 7700s	GC	Volatile sulfur	Dry plasma (GC)	Speciation	^{32}S	91
2021	ICP-QMS/QMS	iCap-TQ	Not available	Uranium ore	Mass shift	Concentration	^{32}S	92
2021	HR-ICP-MS	Element 2?	Not available	Marine sediments	MR (4000)	Concentration	^{32}S	93
2022	HR-ICP-MS	Element XR	Heat-condensing device	Acid solution (50mg->50g)	MR (4000)	Concentration	^{32}S, ^{34}S	94
2022	MC-ICP-MS, ICP-QMS	Nu Plasma 1700, iCAP RQ	LA	Stibnite	Not available	Isotope	^{32}S, ^{33}S, ^{34}S	95
2022	HR-ICP-MS	Element XR?	HPLC	Water	MR (4000)	Speciation	^{32}S, ^{34}S	96
2022	MC-ICP-MS	Nu Plasma 1700	LA	Minerals	HR (10000 to 18000)	Isotope	^{32}S, ^{34}S	97
2022	ICP-QMS/QMS	Agilent 8900	HPLC	Aqua solution	Mass shift	Speciation	^{32}S	98
2022	ICP-QMS/QMS	Agilent 8900	CE	100 mM NaCl	Mass shift	Speciation	^{32}S	99
2022	ICP-QMS/QMS	Agilent 8900	SEC	Water, ammonium citrate buffer	Mass shift	Speciation	^{32}S	100
2022	MC-ICP-MS	Nu Plasma 1700	LA	Resin preserved powder	MR (10000)	Isotope	^{32}S, ^{33}S, ^{34}S	101
2022	Not available	Not available	Not available	Mineral	Not available	Isotope	Not available	102
2022	ICP-QMS/QMS	Agilent 8800?	Not available	Algae	Mass shift	Concentration	^{32}S	103
2022	MC-ICP-MS	Nu Plasma II	LA	Mineral	N_2 mix to Plasma, MR (5000)	Isotope	^{32}S, ^{33}S, ^{34}S	104
2022	MC-ICP-MS	Neptune Plus	LA	Pyrite and chalcopyrite	N_2 mix to Plasma, MR (5000)	Isotope	^{32}S, ^{33}S, ^{34}S	105
2022	ICP-QMS	iCAP-RQ	LA	Sphalerite	O_2 reaction	Not available	^{32}S	106
2022	ICP-QMS/QMS	Agilent 8800	Not available	Semolina	Mass shift	Concentration	^{32}S	107
2022	ICP-QMS/QMS	Agilent 8800	HPLC	β-amyloid	Mass shift	Speciation	^{32}S, ^{33}S, ^{34}S, ^{36}S	108
2023	MC-ICP-MS	Neptune Plus	LA	Minerals, rocks	N_2 mix to Plasma, MR (5000)	Isotope	^{32}S, ^{33}S, ^{34}S	109
2023	MC-ICP-MS	Nu Plasma 1700	LA	Mineral (ZnS)	MR (10000)	Isotope	^{32}S, ^{33}S, ^{34}S	110
2023	ICP-QMS	iCAP-Q	LA	Thin film	O_2 reaction	Concentration	^{32}S	111
2023	MC-ICP-MS	Neptune Plus, Neptune XT	Desolvation device	Acid solution	HR (10000) for ^{32}S, MR for ^{34}S (4000)	Isotope	^{32}S, ^{33}S, ^{34}S	112
2023	ICP-QMS	Agilent 7900	GC	Water and atmospheric sample	Not available	Speciation	^{32}S	113

[a] ICP-QMS/QMS, tandem quadrupole ICP-MS; MC-ICP-MS, multi-collector ICP-MS; HR-ICP-MS, high resolution ICP-MS; ICP-QMS, quadrupole ICP-MS.

[b] AF4, asymmetric flow field flow fractionation; SEC, size exclusion chromatography; LA, laser ablation; GC, gas chromatography; LC, liquid chromatography; HPLC, high performance liquid chromatography; UPLC, ultra performance liquid chromatography; CE, capillary electrophoresis; GPC, gel permeation chromatography; IC, ion chromatography.

Table 2. Manufacturers of ICP-MS instruments and models used for sulfur analysis

Maker of ICP-MS	Model of ICP-MS	Type of ICP-MS
Agilent Technologies	Agilent 7500(x)	ICP-QMS
	Agilent 7700(x,s)	ICP-QMS
	Agilent 7900	ICP-QMS
	Agilent 8800	ICP-QMS/QMS
	Agilent 8900	ICP/QMS/QMS
PerkinElmer	NexION 300(S,D)	ICP-QMS
	ELAN DRC-e	ICP-QMS
	ELAN 6100 DRC II	ICP-QMS
Nu Instruments	Nu Plasma 1700	MC-ICP-MS
	Nu Plasma II	MC-ICP-MS
	Nu Plasma HR	MC-ICP-MS
Thermo Fisher Scientific	X series 2	ICP-QMS
	iCAP-Q(c)	ICP-QMS
	iCAP-RQ	ICP-QMS
	iCAP-TQ	ICP-QMS/QMS
	Element 2	HR-ICP-MS
	Element XR	HR-ICP-MS
	Neptune Plus	MC-ICP-MS
	Neptune XT	MC-ICP-MS

Fig. 3 Hyphenated instruments and research fields for sulfur analysis using ICP-MS. (A) Hyphenated instruments of ICP-MS and number (percentage) of articles and (B) research fields and number (percentage) of articles.

early commercialization of ICP-QMS/QMS. The Nu Instruments share of reports can be attributed to its MC-ICP-MS for isotope analysis. Considering the release of ICP-QMS/QMS by PerkinElmer in recent years and the increasing application of ICP-QMS/QMS in sulfur analysis, the number of reports related to PerkinElmer may increase in subsequent years.

Figure 3 (A) shows that 32% of the articles reported on LA hyphenated ICP-MS, which can be attributed to its elemental imaging capability as well as the direct analysis of solid samples without transfer to a sample solution. Chromatography hyphenated ICP-MS for the chemical species analysis of sulfur accounted for another 31% of the published articles. Desolvation hyphenated ICP-MS for sulfur analysis, which is aimed at avoiding spectral interference from the extremely high density of $^{16}O_2^+$ in the plasma due to the introduction of water, accounts for another 6% of the published articles. A desolvation device, which is located between the nebulizer and the ICP torch, replaces the usual spray chamber in an ICP-MS instrument. The heated chamber in the desolvation device improves the loading efficiency of the sample into the ICP while removing the solvent as vapor, which is exchanged by a countercurrent flow of argon sweep gas. Consequently, desolvation devices can help reduce the signal intensity of $^{16}O_2^+$ by approximately three orders of magnitude and allows the detection of sulfur at the 10 pg/g level using HR-ICP-MS.[117] However, desolvation devices, as compared to the usual spray chamber, have significantly longer paths from the nebulizer to the ICP torch, and a longer washout time may be required to remove the memory effect.

Microwave-assisted combustion and heat-condensing have been hyphenated with ICP-MS for the analysis of coal and acid solution samples, respectively.[22, 96] The use of ICP-MS without a hyphenated instrument accounted for 31% of the published articles, which can be attributed to the fact that ICP-MS was initially an independent elemental analysis instrument. Higher concentrations of sulfur in solution can be directly measured using ICP-QMS by monitoring $^{34}S^+$.[45, 61] The commercial availability of ICP-QMS/QMS improved the capability of detecting sulfur at sub-ng/g levels without using a desolvation device.[81]

Articles related to the use of ICP-MS for sulfur analysis cover research fields such as biology, environment, geology, food/feed, and energy. Figure 3 (B) plots the distribution of articles in different research fields, where sediments and water were treated as environmental samples and minerals and rocks were treated as geological samples. The largest share of 33% (geology) can be partly attributed to the analysis of the sulfur concentration and sulfur isotopes in sulfides.[8, 19, 20, 27, 32, 34, 39, 41, 49, 52] The second largest share of 24% (biology) can be partly attributed to the analysis of sulfur-related proteins and peptides in biological samples.[7, 14, 17, 18, 31, 62, 69, 108] The application of ICP-MS to food and feed samples accounted for 9% of the published reports. The share of 7% (energy) can be attributed to its application in coal-, biodiesel-, petroleum-, and gasoline-related samples.[22, 36, 40, 57, 59, 63, 73, 77] The share of 14% by other samples can be attributed to its application to model solutions and reference materials.

Strategy for spectral interferences. Table 3 summarizes the analytes and related spectral interferences in sulfur analyses using ICP-MS, along with the resolution required for separation. The abundance of each analyte was calculated from the data reported in Ref. [1], whereas the resolution required for the separation was calculated based on the atomic weights reported in Ref. [114].

As shown in Table 3, $^{32}S^+$, $^{33}S^+$, and $^{34}S^+$ could be separated from their typical spectral interference using a resolution of 4000. As summarized in Table 1, measurements in the MR or HR

Table 3. Analytes, typical spectral interferences, and resolution required for separation in sulfur analysis using ICP-MS

Analyte	Nominal mass	Abundance [a]	Typical spectral interference	Resolution required [b]
$^{32}S^+$	32	98.041%	$^{16}O_2^+$	1801
			$^{14}N^{18}O^+$	1061
			$^{14}N^{16}O^1H_2^+$	770
			$^{15}N^{16}O^1H^+$	1040
			$^{15}N^{17}O^+$	1177
			$^{13}C^{18}O^1H^+$	835
$^{33}S^+$	33	0.075%	$^{32}S^1H^+$	3907
			$^{16}O_2{}^1H^+$	1259
			$^{14}N^{18}O^1H^+$	854
			$^{15}N^{18}O^+$	1186
$^{34}S^+$	34	4.196%	$^{33}S^1H^+$	2977
			$^{32}S^1H_2^+$	1711
			$^{16}O^{18}O^+$	1297
			$^{16}O^{17}O^1H^+$	1000
			$^{16}O_2{}^1H_2^+$	904
			$^{15}N^{18}O^1H^+$	866
$^{36}S^+$	36	1.5×10^{-4}	$^{36}Ar^+$	77350
			$^{34}S^1H_2^+$	2186
$^{32}S^{16}O^+$	48	97.807%	$^{48}Ti^+$	2519
			$^{48}Ca^+$	3319
			$^{36}Ar^{12}C^+$	85616
			$^{31}P^{16}O^1H^+$	5041
$^{33}S^{16}O^+$	49	0.075%	$^{49}Ti^+$	2647
			$^{32}S^{16}O^1H^+$	5802
			$^{32}S^{17}O^+$	10140
$^{34}S^{16}O^+$	50	4.186%	$^{50}Ti^+$	2777
			$^{50}Cr^+$	2986
			$^{50}V^+$	3199
			$^{38}Ar^{12}C^+$	999256
			$^{36}Ar^{14}N^+$	6374
			$^{32}S^{16}O^1H_2^+$	2516
			$^{32}S^{17}O^1H^+$	3075
			$^{32}S^{18}O^+$	5913
			$^{33}S^{16}O^1H^+$	4375
$^{36}S^{16}O^+$	52	0.015%	$^{52}Cr^+$	2419
			$^{40}Ar^{12}C^+$	133236
			$^{36}Ar^{16}O^+$	110557
			$^{38}Ar^{14}N^+$	13638
			$^{34}S^{16}O^1H_2^+$	3159

[a] Amount of each analyte was cited or calculated from the isotope data in Ref. [1]

[b] Resolution required (for separation) was calculated using the atomic weights reported in Ref. [113]

mode is commonly used in sulfur analyses using HR-ICP-MS and MC-ICP-MS, which can achieve resolutions exceeding 4000. Furthermore, desolvation devices have been hyphenated with MC-ICP-MS to suppress the formation of oxygen-related interferences.[34, 112] Nitrogen has been mixed with plasma for sulfur analyses using MC-ICP-MS to suppress spectral interferences.[32, 41, 68, 80, 104, 105, 109] Notably, a resolution of 77350 is required to separate $^{36}S^+$ from $^{36}Ar^+$, which cannot be achieved by HR-ICP-MS or MC-ICP-MS.

Monoxide ions, for example, $^{32}S^{16}O^+$, $^{33}S^{16}O^+$, and $^{34}S^{16}O^+$, are often measured using ICP-QMS with oxygen as the reaction gas to avoid spectral interference when measuring $^{32}S^+$, $^{33}S^+$, and $^{34}S^+$.[12, 17, 28, 31, 36, 54-56, 79, 106, 111] The application of oxygen as the reaction gas also contributes to the suppression of argon-related spectral interference.

As summarized in Table 1, mass shift with oxygen as the reaction gas was used for sulfur analysis via ICP-QMS/QMS. In this measurement mode, the first quadrupole mass spectrometer (QMS1) is set to allow the passage of an ion with a *m*/*z* ratio identical to that of a sulfur ion (such as *m*/*z* of 32 for $^{32}S^+$ and $^{16}O_2^+$), which enters the reaction cell and reacts with the oxygen gas. The second quadrupole mass spectrometer (QMS2) is set to allow the passage of an ion (such as *m*/*z* of 48 for $^{32}S^{16}O^+$) with an *m*/*z* larger than that of QMS1 by 16 (that is, the isotope mass of ^{16}O). In this measurement, a sulfur ion (such as $^{32}S^+$) changes to a monoxide ion (such as $^{32}S^{16}O^+$) during transfer to the detector. Because of the high transfer rate (> 90%) from a sulfur ion to its monoxide through a reaction with oxygen gas, this mass shift mode by ICP-QMS/QMS effectively separates a sulfur ion from its spectral interferences without trading off the sensitivity.[115, 116] It should be noted that the measurement of $^{36}S^+$ in the mass shift mode by ICP-QMS/QMS was also reported to evaluate the isotopic composition of ^{34}S-labelled yeast hydrolysate.[108]

Measurands and isotopes for sulfur analysis using ICP-MS. The purpose of sulfur analysis can be classified into the quantitation of concentration, chemical speciation, and isotopic ratio analysis, whose measurements are concentration, species, and isotopes, respectively. Fig. 4 (A) shows the distributions of the measurands in sulfur analyses using ICP-MS. Species and isotopes accounted for 37 and 28% of the articles, respectively, demonstrating the use of sulfur analysis in isotopic and chemical speciation analyses. Nevertheless, determination of the sulfur concentration is also a major topic, accounting for 39% of the articles.

Figure 4 (B) plots the distributions of the isotopes measured for sulfur analysis using ICP-MS, covering all four stable sulfur isotopes (namely, ^{32}S, ^{33}S, ^{34}S, and ^{36}S). Measurements of $^{32}S^+$

Fig. 4 Measurands and isotopes for sulfur analysis using ICP-MS. (A) Measurands and number (percentage) of articles and (B) isotopes and number (percentage) of articles.

were reported in 90% of the articles, with strategies for separating spectral references from $^{16}O_2^+$, such as the O_2 reaction for ICP-QMS, MR for HR-ICP-MS and MC-ICP-MS, and mass shift for ICP-QMS/QMS. An ICP-QMS-based concentration-gradient method permitted the measurement of $\delta^{34}S$ in gypsum samples with a standard deviation of 3.5–13%, providing a relative standard deviation of approximately 18–67%.[48] ICP-QMS/QMS achieved a relative expanded uncertainty (95% confidence interval, $k = 2$) of approximately 0.6% for $\delta^{34}S$ in salmon reference materials.[89] ICP-QMS with O_2 reaction, ICP-QMS/QMS, HR-ICP-MS working at MR, and MC-ICP-MS working at edge mass resolution achieved the best relative standard deviations for $\delta^{34}S$ of 0.26, 0.24, 0.08, and 0.003% respectively.[30]

The measurements of $^{34}S^+$ and $^{33}S^+$ were reported in 64 and 31% articles, respectively, which can be attributed to the fact that the measurement of $^{34}S^+$ is also used for determining the sulfur concentration and chemical speciation analysis,[7, 9, 15, 17, 23, 31, 36, 44, 55, 56, 59, 61, 63, 64, 74, 75, 82, 85, 86, 90, 94, 96, 108] whereas the measurement of $^{33}S^+$ is mainly used for isotopic analyses. Notably, only the $^{34}S/^{32}S$ ratio is required for most isotopic analyses, whereas measuring $^{33}S/^{32}S$ requires extremely high sensitivity owing to the low abundance of ^{33}S.

Only one article reported the measurement of $^{36}S^+$.[108] The difficulty of measuring $^{36}S^+$ can be attributed to both its low abundance (0.01%) and the spectral interference from $^{36}Ar^+$, for which a resolution exceeding 70000 is required for separation.

Detection limit of sulfur. The detection limit is a key parameter for evaluating analytical methods. Table 4 summarizes the detection limits for sulfur analyses using ICP-MS reported in the literature. Notably, the detection limit for ICP-MS depends on the sample introduction rate. Therefore, the values obtained with hyphenated instruments cannot be compared with those obtained without them. The values summarized in Table 4 provide an approximate indication of the sulfur analysis by ICP-MS.

The detection limits obtained by ICP-QMS are 0.126–435 ng/g. An article reported that GC-ICP-QMS achieved a detection limit of 0.0054 ng/g.[91] However, considering the enrichment of the sample (from 1 L to 1 mL) prior to analysis, this detection limit is close to those reported in other articles, that is, approximately 3–8 ng/g.[12, 31, 55, 56, 66, 79] The best reported detection limits for sulfur using ICP-QMS were approximately 0.1–0.3 ng/g, which were achieved with the assistance of a desolvation device or LA.[30, 111] Such low detection limits can be attributed to the suppressed $^{16}O_2^+$ interferences due to the dry plasma condition.

The detection limits obtained using ICP-QMS/QMS range from 0.068 to 290 ng/g. Notably, most articles reported detection limits < 6 ng/g, except for some that were hyphenated with CE, UPLC, HPLC, and LC.[60, 64, 82, 86, 98] The detection limits obtained by HR-ICP-MS were 0.09–500 ng/g, except for some hyphenated with LA, which reported a detection limit > 10000 ng/g.[9, 37] These high detection limits by LA-HR-ICP-MS can be attributed to the analysis of sulfur in large molecules by introducing an extremely small quantity (~30 ng/s) of the sample.[9] The detection limits reported for MC-ICP-MS were 4 and 0.1 ng/g.[16, 30]

In addition to the detection limits given in ng/g or ng/L as summarized in Table 4, detection limits were also reported as 0.3 pg of S by GC-ICP-QMS/QMS,[57] 11 nmol quantum dots/L by AF4-ICP-QMS/QMS,[6] 4, 2, and 1 g of dimethyl sulfide, CS_2, and dimethyl disulfide by GC-ICP-QMS.[113]

The background equivalent concentration (BEC) is another parameter that contributes to the quality of sulfur analysis results obtained using ICP-MS. However, few studies have reported the BEC values. The lowest BEC value of 6 ng/g for sulfur measured using ICP-QMS was achieved with the assistance of a desolvation device.[30] The BEC values reported for sulfur measured using ICP-QMS/QMS were approximately 10–30 ng/g,[60, 78, 107] while hyphenation with a desolvation device helped achieve the lowest BEC value of 3 ng/g.[30] The lowest BEC values reported for the measurement of sulfur using HR-ICP-MS (with a desolvation device) and MC-ICP-MS (with HPLC) were 9 and 20 ng/g, respectively,.[16, 30]

Selected topics of sulfur analysis using ICP-MS

Quantitation of sulfur and related compounds in food/feed samples. ICP-QMS/QMS was used to directly quantify the total sulfur dioxide content in red wine,[15] where the samples were simply diluted with a 5% ethanol solution and injected into the instrument for measurement. A limit of quantification of 10 µg/L was obtained for $^{32}S^{16}O_4^{2-}$. The results obtained with 1/10 to 1/200 dilutions of the sample (SO_2, 150 mg/L) were consistent and independent of the dilution factor, whereas the best precision (approximately 1%, relative standard deviation) was obtained with a 1/200 dilution sample.

The concentrations of sulfur in nine seaweeds were determined using ICP-QMS after acid digestion (0.5 g sample to 50 mL solution), covering a range from 13.15 to 135.13 mg/kg.[65] The sulfur was analyzed by measuring $^{34}S^+$ using 1.5 mL/min helium as a collision gas.

The content of sulfur, as well as chromium, zinc, potassium, and phosphorus, in green alga was determined using ICP-QMS/QMS after acid digestion.[103] The concentration of sulfur in green alga gradually increased from approximately 0.15 to 0.6

Table 4. Sulfur detection limits reported in the published articles

Types	Hyphenated Instrument	Detection limit (ng/g)	Ref. No.
ICP-QMS	Not available	435	60
	LC (O_2 reaction)	8	11
	Desolvation (O_2 reaction)	0.2	29
	Desolvation (He collision)	0.3	29
	HPLC, desovation	3.6	30
	Not available (O_2 reaction)	0.928	53
	IC (O_2 reaction)	3.1	54
	SEC (O_2 reaction)	3.7	55
	LA	7	65
	Not available (O_2 reaction)	6.4	78
	GC	0.0054 (sample concentrated 1 L to 1 mL)	90
	LA (O_2 reaction)	0.126	110
ICP-QMS/QMS	GC	0.068	9
	HPLC	1.5	12
	Not available	1.7	14
	Desolvation	0.2	29
	HPLC	3	30
	Not available	2	58
	CE	267	59
	UPLC	16	63
	Not available	2.814	77
	Not available	0.2	80
	HPLC	67	81
	LC	20	85
	HPLC	290	97
	SEC	6	99
	Not available	2.5	106
	HPLC	0.5 (calculated as 3/10 of limit of quantitation)	107
HR-ICP-MS	LA	10000	8
	Desolvation	23	15
	HPLC	15	20
	Not available	500	25
	Desolvation	0.5	29
	LA	305000	36
	LA	490	43
	GPC	10	58
	Not available	0.09	62
	HPLC	0.1	68
	Not available	11	69
	Not available	0.1	92
	Heat-condensing	1.1	93
	HPLC	160	95
MC-ICP-MS	HPLC	4	15
	Desolvation	0.1	29

pg/cell up to EC_{50} (the concentration of the test sample at which the algae growth rate is reduced to 50%, as compared with the control group), and then significantly decreased.

The sulfur concentration in semolina samples obtained from different durum wheat cultivars were determined using ICP-QMS/QMS after acid digestion (0.1 g sample to 25 mL solution).[107] The concentration of sulfur in the samples was 974–1224 mg/kg, which was discussed, along with 56 other elements, for characterization of the samples.

Determination of sulfur in coal and fuel samples using ICP-MS. Quantification of sulfur in coal samples using isotope dilution (ID-) HR-ICP-MS using microwave-induced combustion for sample pretreatment has been reported.[22] A relative expanded uncertainty < 1.5% was achieved for a nominal mass fraction of 0.5% total sulfur in a coal standard reference material (NIST SRM 2682c). The authors stated that ^{36}S could not be determined using HR-ICP-MS because of the low concentration of ^{36}S and the inability of HR-ICP-MS to separate $^{36}Ar^+$ from $^{36}S^+$.

The sulfur content in biodiesel samples was determined using ID-ICP-QMS after acid digestion (0.25 g sample to 50 mL solution).[36] The sulfur isotopes, that is, $^{32}S^{16}O^+$ and $^{34}S^{16}O^+$, were measured as their monoxide ions by using O_2 as the reaction cell

gas. The concentrations of sulfur in the samples were 0.4–323.8 mg/kg, with relative expanded uncertainties of approximately 50–10%.

The sulfur content in gasoline- and diesel-type samples was determined using HR-ICP-MS after 1/1000 dilution with isopropanol (IPA) and IPA with 10% toluene, respectively.[63] The detection limits for sulfur in different petroleum fuels were 0.12–0.17 ng/g. The sulfur content in the fuel samples was determined to be approximately 5 μg/g with a relative standard deviation of approximately 1%.

Determination of sulfur and related compounds in biological samples. The sulfur content, along with that of phosphorus, in human serum, blood plasma, and whole blood was determined using ICP-QMS after simple dilution in a solution containing 1% HNO_3 and 2% ethanol.[54] Sulfur was measured as its monoxide ion, that is, $^{32}S^{16}O^+$, with O_2 as the reaction cell gas. The detection limit for sulfur was 1.26 μg/L. The concentrations of sulfur in ten samples each of serum, blood plasma, and whole blood were 561.3–791.9, 557.6–925.7, and 1075.6–1609.0 mg/L, respectively.

The sulfur content in different fractions after filtration with 100 and 30 kDa cut-off filters was determined using HR-ICP-MS to study the evolution of protein corona in gold-nanoparticle-treated human serum.[67] Sulfur analyses using HR-ICP-MS were also applied to iron oxide-based nanoparticle-related biomedical research.[70, 87]

Sulfur-related chemical speciation analysis using ICP-MS. AF4-ICP-QMS/QMS was used to study individual populations in nanoparticle–antibody conjugate mixtures and the quantum dot bioconjugation efficiency.[6, 62] Under the optimized operating conditions of AF4, the correlation between the $^{106}Cd^+$ and $^{32}S^+$ peaks contributed to the identification of the conjugation of quantum dots and antibodies.[6] Both the average quantum dot/antibody ratio and the individual populations in the nanoparticle–antibody bioconjugate mixture can be obtained by combining peak area analyses and point-by-point intensity elemental ratio analyses.

CE-ICP-QMS/QMS was used for the direct and simultaneous determination of intra-liposomal and external sulfate in liposomal doxorubicin formulations.[60] Liposome–cisplatin nanosystems and their interactions with transferrin were investigated using CE-ICP-MS/MS by measuring $^{31}P^{16}O^+$ for liposomes, $^{32}S^{16}O^+$ for proteins, and $^{195}Pt^+$ for drugs (cisplatin).[99]

GC-ICP-QMS was used to analyze volatile organic sulfur species from human cadavers and environmental samples.[91, 113] Notably, 1 L of odor sample was actively drawn from a human cadaver at a sampling rate of 100 mL/min through a dual sorbent tube and collected in 1 mL of solution for analysis, that is, an enrichment factor of 1000-fold was achieved for the volatile organic species.[90] GC-ICP-QMS/QMS was used to analyze organosulfur pesticides in food samples and sulfur species in gasoline samples.[10,57] Notably, the sulfur species were measured using GC-ICP-QMS by monitoring $^{32}S^+$, as well as those measured using GC-ICP-QMS/QMS. This can be attributed to the fact that dry plasma conditions result in significantly lower $^{16}O_2^+$ signal intensities, similar to those obtained using a desolvation device with the introduction of a solution.

HPLC-ICP-QMS was used to analyze phosphopeptides and peptides in human plasma.[17, 31] HPLC-ICP-QMS/QMS was used to analyze sulfur species such as proteins, peptides, thiocyanate, xanthates, and amyloid-β.[13, 31, 82, 98, 108] HPLC-HR-ICP-MS was used to analyze sulfur species such as metabolites in mice urine, phosphopeptides, methionine, amyloid-β, and hemoglobin.[16, 17, 21, 69, 96] HPLC-MC-ICP-MS was used to analyze metabolites in mice urine and methionine in human blood plasma.[16, 21] IC, LC, SEC, and UPLC hyphenated ICP-MS methods were also used to determine the sulfur species in other samples.[7, 12, 14, 51, 55, 56, 64, 73, 77, 86, 100] Notably, HPLC-ICP-QMS/QMS achieved a sulfur limit of quantitation of 1.4–9.8 μg/L using a buffer flow rate of 400 μL/min and an injection volume of 10 μL.

LA-ICP-MS for the determination of the sulfur concentration in solid samples. LA-ICP-QMS was used to determine the concentration of sulfur (or used as internal standard) in pea seedlings, pyrite, chalcopyrite, sphalerite, sulfides, magmatic-hydrothermal fluid, glass, minerals, melt inclusions, black shale, human skin, and thin-films.[19, 23, 35, 38, 43, 66, 74, 84, 90, 111] The relatively higher concentrations of sulfur in the samples allowed for sulfur to be analyzed by the measurement of $^{34}S^+$.[23, 74, 90] The dry plasma conditions in LA-ICP-QMS suppressed the formation of $^{16}O_2^+$ interferences and allowed the analysis of sulfur by measuring $^{32}S^+$.[43, 66, 111]

LA-HR-ICP-MS was used to determine the sulfur content in human serum, fluid inclusions, copper, and copper alloys.[9, 37, 44, 85] Transferrin and albumin human serum were quantified by using ID-LA-HR-ICP-MS to measure the sulfur content after polyacrylamide gel electrophoresis separation, which provided a high precision analysis with a low relative uncertainty (~1.5–3%).[9]

LA-MC-ICP-MS analysis of sulfur isotopes in mineral and rock samples. LA-MC-ICP-MS was used to analyze sulfur isotopes in various mineral and rock samples, such as chalcopyrite, sphalerite, pyrite, sulfide, magnetite, pyrrhotite, gelena, stibnite, and zircon.[8, 19, 20, 27, 32, 33, 38, 39, 41, 72, 49, 58, 68, 80, 88, 95, 97, 101, 104, 105, 109, 110]

Reference materials and calibration standards are important in the LA-MC-ICP-MS analysis of sulfur isotopes. Multiple studies have reported the preparation and evaluation of reference materials or standards, including chalcopyrite, sphalerite, sulfide,

and pyrite.[33, 39, 41, 88, 97, 101, 105, 110]

Femtosecond lasers reportedly provide a higher sensitivity and better precision for sulfur analysis than nanosecond lasers under the same instrumental conditions.[32] Such higher analytical performance is attributed to the lower thermal effect and finer particles obtained using femtosecond lasers. Furthermore, a robust plasma condition was achieved using a lower makeup gas flow rate and introducing 4–6 mL/min nitrogen into the plasma, resulting in a significant reduction of the matrix effects.[32] The polyatomic interferences of O_2^+, SH^+, and O_2H^+ were significantly reduced by introducing nitrogen gas to the central gas flow of the plasma, resulting in a broader and flatter interference-free plateau of sulfur isotopes.[27]

Isotope fractionation was reported during the LA process, where lower $\delta^{34}S$ values were obtained at lower raster velocities, larger spot diameters, and larger crater depths.[38] The authors reported that external element standardization or matrix-matched solutions were not recommended for the sulfur isotope analysis of pyrite using LA-MC-ICP-MS due to the inability of cancelling isotope fractionation during LA, regardless of the capability of correcting the mass bias during ICP-MS measurement. Plasma-induced fractionation during sulfur isotope measurements is reportedly due to the valence state difference of sulfur, such as sulfates (S^{+6}) and sulfides (S^{-2}).[8]

LA-MC-ICP-MS was used to analyze sulfur isotopes to characterize the mineralization of lead–zinc, gold, copper–molybdenum–lead–zinc, and antimony deposits,[42, 58, 95, 140, 109] as well as to investigate ore-forming processes.[19, 49]

CONCLUSIONS

The use of ICP-MS for analyzing sulfur has been reported in the fields of geology, biology, environment, food/feed, and energy. All ICP-MS types, that is, ICP-QMS, ICP-QMS/QMS, HR-ICP-MS, and MC-ICP-MS, are widely used to analyze sulfur and, depending on the hyphenated instruments or operating conditions, are capable of detecting sulfur at the sub-ng/g level. LA, chromatography, and desolvation have been combined with ICP-MS for the direct analysis of solid samples, chemical speciation analyses, and suppression of oxygen-related spectral interference, respectively.

LA-MC-ICP-MS has been widely used for the isotope analysis of sulfur, covering the preparation and evaluation of reference materials, laser ablation- and plasma-induced isotope fractionation, and application in geological samples for studying mineralization and ore-forming processes.

Notably, the application of ICP-QMS/QMS (regardless of its later availability than other types of ICP-MS) in sulfur analysis accounted for over 20% of the published articles, which can be attributed to the advantages of reducing oxygen-related spectral interference using mass shift mode measurements with O_2 as the reaction gas.

The direct introduction of a solution into ICP-QMS/QMS reportedly facilitates the analysis of sulfur isotopes, providing accuracy and precision for $\delta^{34}S$ that is comparable to those obtained using MC-ICP-MS.[71, 83, 89] The application of LA-ICP-QMS/QMS for sulfur isotope analysis is expected to increase in the near future.

The detection limit for sulfur analysis using ICP-MS is as low as the subparts-per-billion level. These low concentrations may be the margins of commercial instruments.

Spectral interference is one of the key challenges in sulfur analysis using ICP-MS. Mass shift with O_2 as the reaction gas was shown to be effective in ICP-QMS/QMS, providing sufficient spectral separation without an apparent tradeoff in sensitivity. MC-ICP-MS with a reaction cell has recently become commercially available and is expected to provide a substantially better sulfur isotope analysis performance in the near future.

Time-of-flight ICP-MS is an emerging type of ICP-MS capable of simultaneously measuring large numbers of elements, and its application in single-cell or single-particle analyses of sulfur-containing analytes is expected to increase.

AUTHOR INFORMATION

Yanbei Zhu received his PhD in March of 2005 from Nagoya University. He joined NMIJ/AIST in April of 2007 and started the research on development of certified reference materials (CRMs) and related techniques for elemental analysis in food and environmental samples. Yanbei is focusing on quantitative elemental analysis based on ICP-MS related techniques, as well as development of devices and instruments fascinating the sample pretreatment process and on-site analysis.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI Grant Number JP22K05181.

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