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Review

Sulfur analysis by inductively coupled plasma-mass spectrometry: A review

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ABSTRACT

In recent years the number of applications of sulfur (S) analysis using inductively coupled plasma mass spectrometry (ICP-MS) as detector has increased significantly. In this article we describe in some depth the application of ICP-MS for S analysis with emphasis placed on the sulfur-specific detection by hyphenated techniques such as LC, GC, CE and LA coupled on-line to ICP-MS.

The different approaches available for sulfur isotope ratio measurements by ICP-MS are also detailed. Particular attention has been paid to the quantification of peptides/proteins and the analysis of metallopeptides/metalloproteins via sulfur by LC–ICP-MS. Likewise, the speciation analysis of metal-based pharmaceuticals and metallodrugs and non-metal selective detection of pharmaceuticals via S are highlighted. Labeling procedures for metabolic applications are also included. Finally, the measurement of natural variations in S isotope composition with multicollector ICP-MS instruments is also covered in this review.

Contents

Abbreviations: API, active pharmaceutical ingredient; capLC, capillary liquid chromatography; CC, collision cell; CE, capillary electrophoresis; Cys, cysteine; DRC, dynamic reaction cell; ETV, electrothermal vaporization; GC, gas chromatography; HPLC, high performance liquid chromatography; ICP-MS, inductively coupled plasma mass spectrometry; IDMS, isotope dilution mass spectrometry; IRMS, isotope ratio mass spectrometry; LA, laser ablation; LC, liquid chromatography; MC-ICP-MS, multicollector ICP-MS; Met, methionine; MT, metallothionein; ORS, octapole reaction system; Q-ICP-MS, quadrupole ICP-MS; RC, reaction cell; SEC, size exclusion chromatography; SF-ICP-MS, sector field ICP-MS; UPLC, ultra performance liquid chromatography; V-CDT, Vienna-canyon diablo troilite.

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1. Introduction

Sulfur-containing compounds are ubiquitous both in the environment and in biological materials and, therefore, the detection of sulfur can be applied in many fields such as peptide/protein analysis, pharmaceutical research (drugs and metabolites), industrial analysis (petroleum matrices and steels), and environment analysis (pesticides). Sulfur (S) has four stable isotopes at nominal masses of 32, 33, 34 and 36, with representative isotopic composition of 94.99 (26), 0.75 (2), 4.25 (24) and 0.01 (1) %, respectively [1]. Isotopes of S are fractionated by various chemical, physical, and biological processes and therefore the uncertainty on the atomic weight of this element is assigned largely on the basis of natural variability [2]. For sulfur, the atomic weight is now defined as the range [32.059; 32.076] by the IUPAC [2]. In recent years, the ICP-MS technique has matured from being known as only a "metal" detector to become capable of detecting most of the elements present in the periodic table. For S elemental and isotope analysis, this trend has been especially boosted by the availability of collision and reaction cells and more robust HR-ICP-MS instrumentation, as well as the development of suitable interface technologies for the coupling of separation techniques to ICP-MS. The significant expansion in this topic is reported in Fig. 1 where the number of peer-reviewed papers in the Web of Science® database published between 1998 and 2014 that deal with S analysis by ICP-MS (search terms: sulfur and ICP-MS) is shown.

The high first ionization potential of sulfur (10.357 eV) leads to a relatively low ionization efficiency in an argon-based plasma. In addition, S is relatively light and thus is not transmitted by typical instrumental ion optics as effectively as heavier masses. As a result, current ICP-MS is expected to achieve DL for sulfur in the parts-per-billion range. The main spectral interferences when measuring sulfur stable isotopes by ICP-MS are reported in Table 1. Despite the fact that S detection is hampered by spectral interferences which are formed inside the plasma (mainly oxygen dimmers), different approaches can be found in the literature regarding S isotope analysis as commented below for total S determinations by ICP-MS.

Herein, following the remarkable work of N. Jakubowski et al. regarding the speciation of sulfur [3] we describe in some depth the application of ICP-MS for S analysis with emphasis placed on the S-specific detection and isotopic analysis in hyphenated techniques such as HPLC, GC, CE and LA coupled on-line to ICP-MS.

Table 1
Main spectral interferences when measuring sulfur by ICP-MS at sulfur isotopes and sulfur oxide ions.

Analyte	Abundance (%)[a]	Nominal mass	Spectral interference	Resolution[b] (m/Δm)
$^{32}S^+$	94.99 (26)	32	$^{16}O^{16}O^+$	1801
			$^{14}N^{18}O^+$	1061
			$^{15}N^{16}O^1H^+$	1040
			$^{14}N^{16}O^1H_2^+$	770
$^{33}S^+$	0.75 (2)	33	$^{32}S^1H^+$	3907
			$^{16}O^{16}O^1H^+$	1259
			$^{14}N^{18}O^1H^+$	854
			$^{15}N^{18}O^+$	1186
$^{34}S^+$	4.25 (24)	34	$^{33}S^1H^+$	2977
			$^{32}S^1H_2^+$	1711
			$^{16}O^{18}O^+$	1297
			$^{16}O^{17}O^1H^+$	1000
			$^{16}O^{16}O^1H_2^+$	904
			$^{15}N^{18}O^1H^+$	866
$^{36}S^+$	0.01 (1)	36	$^{36}Ar^+$	77,350
$^{32}S^{16}O^+$	94.76 (26)	48	$^{48}Ti^+$	2519
			$^{48}Ca^+$	3319
			$^{36}Ar^{12}C^+$	85,616
			$^{31}P^{16}O^1H^+$	5041
$^{33}S^{16}O^+$	0.78 (2)	49	$^{49}Ti^+$	2647
$^{32}S^{17}O^+$			$^{32}S^{17}O^+$	10,140
$^{34}S^{16}O^+$	4.43 (24)	50	$^{50}Ti^+$	2777
$^{32}S^{18}O^+$			$^{50}Cr^+$	2986
			$^{50}V^+$	3199
			$^{38}Ar^{12}C^+$	999,256
			$^{36}Ar^{14}N^+$	6374
			$^{32}S^{18}O^+$	5913
			$^{33}S^{17}O^+$	6400

[a] The isotope composition for sulfur was taken from reference [1]. The values in brackets are the uncertainties given based on the natural variability. The abundances for SO were calculated with the known isotope composition of sulfur and oxygen and the uncertainties based on their natural variability.

[b] For SO the resolution was calculated for the most abundant ions at nominal masses 49 and 50 ($^{33}S^{16}O$ and $^{34}S^{16}O$ respectively).

2. Instrumentation for the determination of sulfur by ICP-MS: resolving spectral interferences

2.1. Quadrupole based ICP-MS instruments

Using single quadrupole ICP-MS technology, ^{36}S cannot be monitored due to the fact that $^{36}S^+$ is irresolvable from the elemental isobar

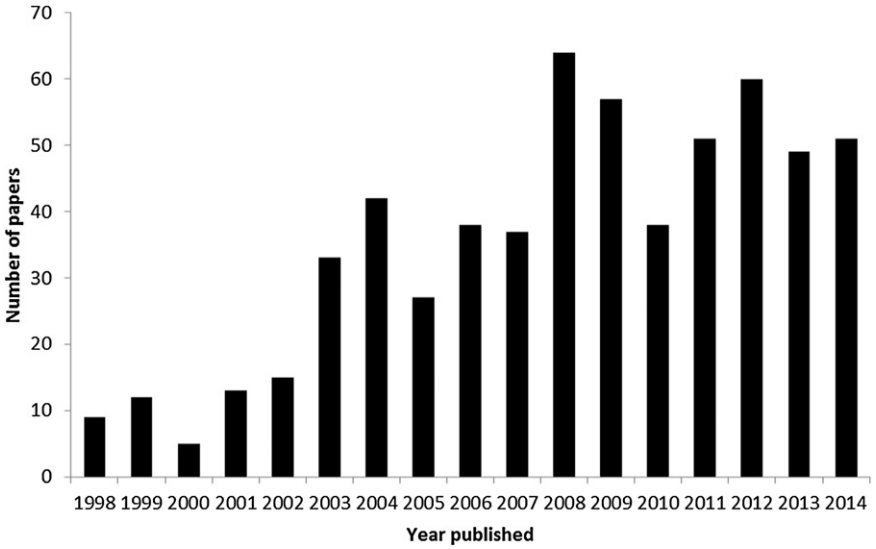

Fig. 1. Number of peer-reviewed papers listed in the Web of Science® database over the last 15 years on sulfur analysis by ICP-MS (search terms in topic: sulfur and ICP-MS).