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Review

Trends in selenium determination/speciation by hyphenated techniques based on AAS or AFS

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Abstract

The field of selenium speciation has been studied for decades and the growing interest in this field seems never to reach a plateau. Although powerful techniques based on mass spectrometry are nowadays used for selenium determination/speciation, few laboratories can support the high cost of such techniques. The hyphenation of chromatography to atomic absorption or atomic fluorescence spectrometry (AAS or AFS) is still a reliable and low-cost alternative for routine laboratories. In this work we present the most important parameters dealing with selenium speciation along with the latest trends in this subject, namely in the items related with sample treatment and hyphenation techniques with AAS and AFS detection.

Keywords: Selenium speciation; Hyphenated techniques; AAS; AFS

Contents

1. Introduction

Research in Se speciation is still an attractive area since, on the one hand, lower detection limits can be achieved with recent powerful analytical tools, such as ICP–MS or LC–MS–MS and, on the other hand, there are several Se-containing organic molecules that remain unidentified. In addition, the total role of Se-proteins, i.e. metabolism or antioxidant properties, in living organism is far from being fully understood [1]. Although modern techniques using mass detection can help to a better understanding of the experimental data and to almost certain

Abbreviations: AAS, atomic absorption spectrometry; AFS, atomic fluorescence spectrometry; DEDSe, diethyl diselenide; DESe, diethyl selenide; DMDSe, dimethyl diselenide; DMSe, dimethyl selenide; EH, enzymatic hydrolysis; EPS, enzymatic probe sonication; ET–AAS, electrothermal atomic absorption spectrometry; HG, hydride generation; HHPN, hydraulic high pressure nebuliser; HIFU, high intensity focused ultrasound; LC, liquid chromatography; MAAL, microwave assisted acid leaching; MD, microwave digestion; SeCyst, selenocystine; SeEt, selenoethionine; SeMet, selenomethionine; SS, slurry sampling; $TMSe^+$, tri-methyl-selenonium; UB, ultrasonic bath; USAL, ultrasonic assisted acid leaching; UV, ultraviolet

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species identification, many analytical laboratories cannot support such equipment because of their high price and expensive maintenance. Hence, alternatives for Se speciation in routine laboratories are mandatory. The hyphenation of common techniques such as chromatography and atomic absorption or fluorescence spectrometry (AAS or AFS) is a substitute of mass spectrometry (MS) techniques of great interest. As Fig. 1 shows, the main aim of the present work is to provide a rapid overview of the actual trends in Se determination from solid biological samples by the aforementioned hyphenated techniques along with (i) methodologies used for Se preservation in standards and sample extracts, (ii) modern sample treatments for total Se extraction and speciation from solid samples, and (iii) current procedures for Se species separation, degradation, and quantification.

2. Preservation/stability of standards and treated samples

The stability of Se species in standards and environmental samples is an issue of primary importance in order to obtain accurate results. Thus, sampling and storage affect the reliability of the results since volatilisation, adsorption, inter-conversion of species, precipitation or contamination may change the Se composition of the sample. Data reported in the literature mention the following parameters to be taken into account with aqueous samples to avoid Se losses: pH, ion strength, container material and ratio of container surface area per unit of volume [2]. However, as can be seen in Table 1, there is no agreement in the literature for Se standards preservation conditions. It seems that light does not have a significant effect on inorganic selenium species [3]. Inorganic Se solutions were preserved when acidified at pH 1.5 with H_2SO_4 in polyethylene or pyrex containers at room temperature [4]. As a general trend, Se(IV) solutions should be acidified whilst Se(VI) should not be. The later specie remained unaltered for a period of ca. 1 year under the aforementioned

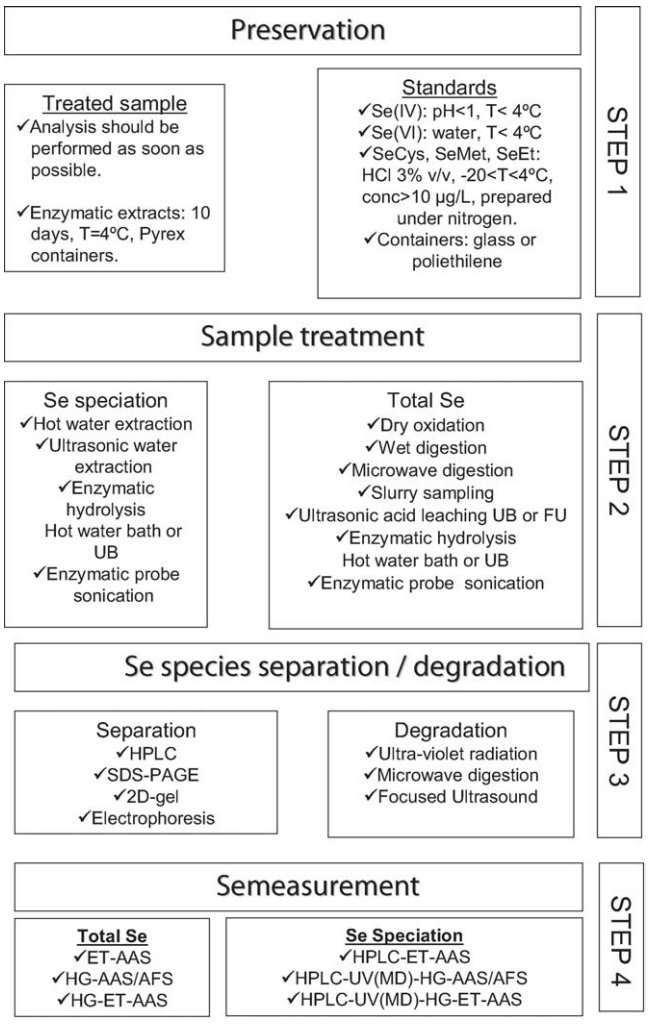

Fig. 1. Comprehensive scheme for Se determination/speciation by hyphenated techniques with atomic absorption or atomic fluorescence spectrometry.

Table 1
Selenium standards preparation and preservation

Selenium species	Analytical technique	Comments	Reference
Se(IV), Se(VI), Se–DL–Met	LC–HG–AAS	All standards were prepared in Milli-Q water. Stock solutions were stored in a freezer at −20 °C	[44]
Se(IV), Se(VI), Se–DL–Met, Se–Et, $TMSe^+$	FI–HG–AAS	All standards were prepared in Milli-Q water. Stock solutions were stored in a freezer at −20 °C. Total Se determination after microwave digestion	[41]
Se(IV), Se(VI)	FI–HG–ET–AAS	Se(IV) and Se(VI) were prepared in HCl 1.2 M	[42]
Se(IV), Se(VI)	FI–HG–AAS	Se(IV) and Se(VI) were prepared in sulphuric acid pH 0	[43]
Se–Met, Se–Et, Selenoprotein P	ET–AAS	Se–Met was dissolved in 0.14 M HNO_3 whereas Se–Et was dissolved in water. Selenoprotein P was obtained from human plasma after purification	[31]
Se(IV), Se(VI)	HG–AAS	Se(IV) and Se(VI) were prepared in HCl 10% (v/v) and in water, respectively	[45]
Se(IV), Se(VI), Se–DL–Met, Se–DL–Cys	HG–AAS and HG–AFS	Se(IV) was dissolved in 1 M HNO_3; Se(VI) was prepared in water. Se–DL–Met, Se–DL–Cys were prepared in HCl 3% (v/v)	[8]
Se(IV), Se(VI), Se–DL–Met, Se–DL–Cys, $TMSe^+$	HG–AAS	All standard solutions were prepared in water. Spiked selenium species in urine, Se(VI), SeMet and $TMSe^+$ were stabled in pre-cleaned urine (C_{18} cartridges) for 48 h	[7]
Se(IV), Se(VI), Se–DL–Met, Se–DL–Cys, $TMSe^+$	HG–AFS	Se(IV), Se(VI), trimethylsenonium, were prepared in water; Se–DL–Met and Se–DL–Cys were weighed under nitrogen and dissolved in HCl 0.5% (v/v)	[12]

conditions [5]. The substances present in solution may affect selenium species stability. Thus, Se content in seawater samples acidified with HCl (pH 2) and stored in glass or polyethylene containers was stable for at least 4 months [6]; Se(VI), SeMet and $TMSe^+$ were stable in pre-cleaned urine (C_{18} cartridges) for only 48 h [7], whereas enzymatic extracts of oyster tissues were stable when stored in pyrex containers for a maximum of 10 days at 4 °C, in the latter conditions SeMet and $TMSe^+$ were preserved [8]. It is always necessary to bear in mind that the acid chosen to preserve Se solutions must not interfere with the analytical method and as a general trend, acidification with HCl is recommended. Temperature is a trade-off for inorganic selenium species, and Se(IV) and Se(VI) solutions should be stored at temperatures as low as possible, e.g. −20 °C [3]. Concerning organic selenium species, recent literature reports SeMet and SeCys solutions dissolved in HCl 3% (v/v) [8,9]. As a role, standard concentrations of SeMet should be >10 μg L^{-1}, prepared in a high ionic strength and stored in glass or polyethylene containers, otherwise degradation of SeMet solutions is observed [10]. Volatile Se organic species are difficult to handle and store, since compounds such as DMSe, DESe, DMDSe and DEDSe were found highly unstable, even being stored at −20 °C in the dark [11]. For the preparation of SeMet and SeCys, Sabe et al. [12] have proposed to weigh the sample under nitrogen to prevent sample degradation and dissolving the sample in HCl 0.5% (v/v).

3. Se extraction from solid matrices

3.1. Extraction procedures for total Se

Vassileva et al. have suggested classical sample treatments, that is, dry oxidation and wet digestion, for total Se quantification [13] in terrestrial plants. However, in the aforementioned work, the authors compare dry oxidation and wet digestion with slurry sampling (SS) concluding that the SS procedure for ET–AAS gives consistent results regardless of the sample type studied (plant, algae, sediment, soil). In addition, similar results were obtained for soil and sediment samples, when comparing SS in an HNO_3/H_2O_2 liquid media with the classic wet digestion method performed with different acid mixtures with HF, demonstrating that to achieve total Se determination HF is not necessary in the aforementioned matrices. When possible, handling of HF should be avoided owing to its highly toxic properties. As shown in Table 2, some interesting works dealing with comparison of Se extraction procedures from biological samples, focused on total selenium determination have been developed. For instance, Bermejo-Barrera and co-workers [14] compared five different sample treatments using chemometrics: microwave digestion (MD), SS, ultrasonic assisted acid leaching (USAL), microwave assisted acid leaching (MAAL) and enzymatic hydrolysis (EH). They found that MD, MAAL and SS provided the best results. Interestingly, the previous work does not refer those problems dealing with Se ultrasonic acid assisted extraction that were reported by Méndez et al. [9], namely Se re-absorption in the sample as a function of the HNO_3 concentration used in the extraction procedure. This work reported successful Se extraction from lichen and mussel tissue with HIFU in HNO_3 1% (v/v) solution in 4 min. The procedure was compared against microwave digestion giving better performance. The analysis of selenium in hair samples must be done with a dedicated sample procedure, since it was found that hair cleaning with (i) acetone/methanol, (ii) water + bath sonication, (iii) Na lauryl sulphate, or (iv) acetone/H_2O caused Se losses of ca. 13, 10, 9, and 5%, respectively [15].

3.2. Extraction procedures for Se speciation

The identification and quantitative determination of the chemical forms of metals in foods or biota presents several challenges. The extraction and the separation steps must be carefully considered in order to maintain the integrity of the metal species. Extraction conditions must be chemically mild but sufficiently efficient to liberate the species from the matrix. Common methodologies for Se speciation are enzymatic and basic hydrolysis, the former being the most widely used. Traditional Se enzymatic digestion for speciation is a time-consuming approach, far from being quantitative and with a risk of selenium inter-conversion [16]. Those procedures with enzymes have been performed with incubation in bath at 37 °C or with bath sonicaton, the later being less time-consuming than the former. The following matrices were subjected to traditional enzymatic digestion with a different degree of success (see Table 2 for details): selenium-enriched yeast [17]; edible mushroom [18], or Brazil nuts [19].

Advanced oxidations processes for sample treatment in atomic spectrometry have been recently described in detail [20]. Despite of their inherent environmental advantages along with their easy implementation, little efforts have been done by the analytical community to develop new methodologies using UV radiation, ultrasonication or ozonation for chemical speciation from solid samples. The reason may lay in the fact that, apparently, these kinds of methodologies are time-consuming, when comparing them with other traditional approaches, for example, involving chromatographic separations. Other modern approaches such as pressurised liquid extraction (PLE) have been successfully tried for the extraction of selenocompounds from yeast material. Thus, Gómez-Ariza et al. [21] have reported the extraction, separation and determination of the following species using PLE: SeCys, SeMet, SeEth, Se(IV) and Se(VI) from yeast material.

4. Se species separation/degradation and Se measurement

Speciation of selenocompounds requires (i) separation with an appropriate technique, (ii) destruction of the organocompund, and (iii) selenium quantification. As far as separation is concerned, Se speciation has been done with different chromatographic approaches. For instance, anionic chromatographic columns have been used to separate Se(IV) and Se(VI) [22] or Se(IV), Se(VI) and $TMSe^+$ [23]. Organic cationic forms of Se, such as $TMSe^+$, dimethylselenocysteineselenonium, methylselenomethionineselenonium, Se-methylselenocysteine

Table 2
Selenium extraction/separation methodologies

Matrix	Selenium species/determination	Extraction methodologies/Remarks	Reference
Selenized yeast	SeMet; SeCys/speciation	LC–ET–AAS. Se determination, total and speciation. Five extraction procedures: (i) mineralization with $HNO_3 + H_2O_2$ gives total content, (ii) enzymatic hydrolysis yields 92 ± 1% Se extraction (10 mg sample/100 mg protease, medium phosphate–citric acid buffer with a 7.5 pH, stirred for 24 h in water bath at 37 °C), (iii) warm water extraction (100 mg) with 5 h shaking yields 20% of total selenium, (iv) organic extraction (100 mg, 2:3:5 water:chloroform:methanol) with 5 h shaking yields 11 ± 2% Se extraction and (v) acid hydrolysis (50 mg + 1.5 ml of 6 M HCl, stirred for 5 h in a water bath) yields to 8 ± 0.2% Se extraction. Major selenium species present: selenomethionine, 42% and selenocystine 35%. The separation was achieved by ion-pairing chromatography using sodium heptanesulphonate as the anionic counter-ion. Pd used as matrix modifier.	[17]
RM: whole meal flour, whole milk spinach leaves, poplar leaves, human hair	Se(IV), Se(VI)/total selenium	Total selenium determination after MD with HNO_3 and H_2O_2. NO_x interferences in Se determination by AAS were avoided with amidosulfuric acid.	[35]
Industrial sewage sludge	Selective determination of Se(IV) in the presence of Se(VI)	Sample was MW digested with HNO_3 and HF. Se(IV) was derivatizated with $NaBEt_4$ and trapped in a graphite tube (ET–AAS).	[42]
Plastic membranes	Selenoproteins/speciation	Direct determination of Se in selenoproteins by ET–AAS in plastic membranes after protein separation by gel electrophoresis.	[31]
Powdered milk	Total selenium	Determination by HG–AFS. Slurry preparation. One-gram sample plus aqua regia plus 10 min bath sonication. Reducing agent: $NaBH_4$, 1.2% (w/v), 4.5 ml/min. Carrier: HCl 4.5 mol/L, 9 ml/min.	[46]
Seafood samples	Total selenium	Determination by ET–AAS (i) MW digestion: 0.2 g sample + HNO_3 + H_2O_2; (ii) slurry sampling; (iii) UB leaching: 0.2 g sample + HNO_3 + HCl + H_2O_2; (iv) MW leaching: 0.2 g sample mass + HNO_3 + HCl + H_2O_2; (v) enzymatic hydrolysis. Similar results with i–iv.	[14]
Seafood samples	Total selenium	Determination by ET–AAS. Extraction with focused ultrasound in acidic media: 3 min, 50% amplitude, 0.5% (v/v) HNO_3. Se re-absorption in the sample as function of the acid concentration.	[9]
Model solutions	Se(IV), Se(VI), Se–DL–Met, Se–DL–Cys/speciation	Determination by FI–HG–AAS. Mild sample pre-treatment procedures for determination of Se species after photolytic and sonolytic treatments. Four analytical schemes: (i) pH 0.4 (HCl), Se(IV); (ii) pH 0.4 (HCl) plus UV 45 min, Se(IV) + Se(VI) + SeMet + SeCys; (iii) pH 0.4 with HCl plus US at 25% amplitude, 25 min, Se(IV) + SeCys; (iv) pH 0.4 with HCl plus 10E4 mg/L KNO_3 and UV 45 min, Se(IV) + SeMet + SeCys.	[47]
Edible mushroom	SeCys, SeEt, Se(IV), Se(VI)/speciation	LC–HHPN–AFS. Separation performed on a LiChroCART 125-4 column packed with 5 μm LiChrospher RP-18. Enzymatic digestion procedures with pepsin, trypsinand pronase. Sample diameter <125 μm. Five different sample procedures. None of the three proteolytic enzymes in isolation was able to produce over 64% extraction. Sequential enzymatic digestion gave better performance than one-step enzymatic digestion.	[18]
Brazil nut	SeCys, SeMet, total Se	LC (ion pairing and anion-exchange)–UV–HG–AFS. Preparation of a reference material. Lipid removal with soxhlet distillation with cyclohexane. Especiation: pronase E, 15 mg, plus 150 mg sample + phosphate buffer (pH 7.4) + stirring 24 h at 37 °C. Total: 150 mg sample + 2 mL concentrated HNO_3 + 2 mL concentrated H_2O_2 + 12 h contact time + 20 min in a microwave oven.	[19]

and SeMet have been separated with cationic columns [24]. Separation of seleno–aminoacids has been achieved by reverse-phase columns [25]. Five selenium species, SeCys, SeMet, SeEth, Se(IV) and Se(VI), were separated in an elegant manner and determined in extracts from yeast material by LC–MD–HG–AFS [21] using a column-switching system that coupled reversed-phase and ion-exchange columns in the same on-line system. Two chromatographic techniques were used by connecting reverse-phase C-18 and ion-exchange columns in series to separate Se(IV), Se(VI), SeMet and SeCys [26]. Gomez-Ariza et al. have shown that LC–MD–HG–AFS has better performance than LC–ICP–MS for the determination of SeMet in breast and formula milk [27]. The latter work is also related with chiral SeMet speciation.

Concerning destruction/quantification of the Se organocompounds, this can be done by direct introduction of the chromatographic eluate containing the Se specie into the graphite furnace (LC–ET–AAS) or by on-line transformation into Se(IV) and reduction to H_2Se with different procedures such as those using $K_2S_2O_8$–NaOH [23], $KBrO_3$–HBr [28] or KBr–HCl [29]. These on-line procedures need the aid of microwave or ultraviolet heating (LC–UV(MO)–HG–AAS/AFS). Selenium can

be also determined by formation of the hydride and trapping into a graphite furnace [30] (FI–HG–ET–AAS), which helps to achieve lower detection limits. Selenoproteins were also separated by gel electrophoresis in bands that later were excised for selenium quantification by ET–AAS [31].

Direct determination by ET–AAS of Se solutions with high organic content was found troublesome. Thus, different sensitivities were obtained for human blood plasma spiked with different Se-species: Se(IV) = Se(VI) > SeMet > $TMSe^+$ when the Se content was quantified by ET–AAS [32]. In addition, Sabe et al. [12], found that the accurate Se determination in 1/5 diluted serum was only possible with the standard addition method, needing an analysis time of 45 min per sample. Thus, when working with ET–AAS and solutions with high organic matter content, analysts are encouraged to perform recovery studies spiking the samples with different Se-species. Different matrix modifiers have been proposed for Se determination with eletrothermal atomisation such as Pd [47], Ir + Rh, Pd + Mg [33] or Ir + Zr [30]. Concerning total determination with hydride generation from all the selenium species, only Se(IV) forms the volatile selenium hydride, H_2Se. For this reason transformation of the different Se compounds into Se(IV) prior to hydride formation is mandatory. Usually, Se(VI) is transformed into Se(IV) by using HCl 6 M, or HCl 1 or 2 M with heating in on-line or off-line procedures [15,34]. When microwave digestion is used for sample decomposition using nitric acid, an important source of interference is nitrite that is formed by the oxidative decomposition with nitric acid and it forms NO_x through acidic disproportionation and nitrosilchloride by reaction with HCl. These intermediates may cause a drastic signal depression due to their interaction with H_2Se [35]. To overcome this problem, different approaches have been reported in literature, namely the use of the reagents urea [36], or amidosulfuric acid [35]. The application of sulphanilamide is also found in the literature but it is limited to batch systems, since insoluble by-products would block the sensitive FI systems [35]. Moreno et al. [37] have reported that accurate determination of Se(IV) by hydride-generation is not possible if some organic species, such as DMSe or DMDSe are present. This is due, like Se(IV), to the formation of volatile species when they react in acid media with sodium borohydride.

4.1. Future trends

Recent trends in sample treatments for Se extraction from biological matrices suggest the hyphenation between high intensity focused ultrasound (HIFU), and enzymatic procedures, like the ultimate goal for total Se extraction, preserving Se species integrity. The methodology has been named enzymatic probe sonication (EPS). Concerning total extraction with EPS, Se was extracted from selenized yeast, oyster and mussel tissues, using HIFU in conjunction with the enzyme Protease XIV in a time as short as 15 s [38]. This methodology was later validated for Se extraction from yeast by Sanz-Medel and co-workers [39]. Nevertheless, the total Se determination was performed with ICP–MS, hence it is expected more research in this area, since little has been done to expand this methodology to other kind of techniques, such as UV–HG–AAS/AFS or UV–HG–ET–AAS. As far as Se speciation with EPS concerns, total Se–Met was recovered in 30 s of sonication in yeast [38]. This new procedure, EPS, matches the minimalism concepts: low volume, 1 ml, and low sample and reagent masses, 20 and 10 mg, respectively. Furthermore, Cabañero et al. [40] have reported the successful Se speciation in chicken muscle, liver, kidney and feed with a treatment time of 2 min using EPS. Although this new sample treatment is a promising methodology, it has been only assessed, to the best of our knowledge, for its application in LC–ICP–MS. Hence, it is expected in the near future the development of this methodology for its applications in AAS or AFS, especially for speciation with on-line hydride generation systems.

Méndez et al. [47] have recently developed a work in which different Se species were identified in model waters, using ultraviolet radiation and focused ultrasounds in the sample treatment. However, the identification of Se(IV), Se(VI), Se–Met and Se–Cys needed four different sample treatments with a total time involved of about 115 min, which is by far more than the time needed to perform a separation of the same species using chromatography. In addition, focused ultrasound was applied for a time as long as 25 min, which is too much for an ultrasonic probe, causing the fast deterioration of the probe tip as consequence of the continuous mechanical stress. In addition, the total concentration of the different species was obtained by subtraction among the four treatments used in the whole procedure; the robustness of this approaches being severely affected by the concentration levels of the different species. Nevertheless, these procedures are promising methodologies that deserve more research in order to reduce the total steps and time involved in the speciation attempt and, over all, the efforts of the analytical community must be focused on the application of procedures such as the one above referred to solid biological samples.

5. Conclusions

Se(IV) must be preserved acidified at pH < 2, preferably with HCl, although other acids may be used. Se(VI) must be stored unacidified. Concerning organic Se, Se–Met and Se–Cys, solutions should be prepared in HCl solution ranging 0.5–3% (v/v) and under nitrogen. Solutions should be stored at the lowest temperature possible in polyethylene containers.

Se extraction from solids for total quantification could be still done with the classic wet or dry digestion methods, although those procedures have been overcome by modern treatments such as slurry sampling, microwave acid digestion/leaching, ultrasonic assisted leaching with bath or probe and the more recent hyphenation between focused ultrasound and enzymes, namely EPS. The later methodology seems to be a reliable and fast approach for Se speciation, and more research is expected in this area.

Se species determination can be actually done in such a way, that cationic and anionic selenocompounds can be separated in the same on-line procedure using two different chromatographic columns.

As far as destruction of isolated organoseleno compounds is concerned, different approaches can be used in on-line or off-line procedures. Hydride generation in conjunction with

electrothermal atomisation remains an interesting approach that deserves more research, since on the one hand, it can be hyphenated to LC and, on the other hand, detection limits of the same order than those obtained with mass techniques can be achieved.

As a final remark, EPS can be easily adapted to on-line procedures. Bearing in mind that selenium can be extracted not only partially but totally with this approach; Se levels in extracts from biological samples are going to rise up until the detection limits achieved with the hyphenated techniques here reported, which is going to open new possibilities for routine selenium speciation with instrumental couplings based on AAS or AFS. Although the time needed to perform an analysis with the hyphenated methodologies is higher than the one with the mass spectrometry-based approaches, most routine laboratories can support the former but not the latter analysis system.

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References

[1] C.W. Nogueira, G. Zeni, J.B.T. Rocha, Chem. Rev. 104 (2004) 6255.
[2] R.M. Olivas, O.F.X. Donard, C. Camara, P. Quevauviller, Anal. Chim. Acta 286 (1994) 357.
[3] M.G. Cobo, M.A. Palacios, C. Camara, F. Reis, P. Quevauviler, Anal. Chim. Acta 286 (1994) 371.
[4] V. Cheam, H. Agemian, Anal. Chim. Acta 237 (1980) 237.
[5] J.L. Gómez-Ariza, E. Morales, D. Sanchez-Rodas, I. Giraldez, Trac. Trends Anal. Chem. 19 (2000) 200.
[6] C.I. Measures, J.D. Burton, Anal. Chim. Acta 237 (1980) 177.
[7] M.M. Gomez, T. Gasparic, M.A. Palacios, C. Camara, Anal. Chim. Acta 374 (1998) 241.
[8] P. Moreno, M.A. Quijano, A.M. Gutiérrez, M.C. Pérez-Conde, C. Cámara, Anal. Bioanal. Chem. 374 (2002) 466.
[9] H. Méndez, I. Lavilla, C. Bendicho, Anal. Chim. Acta 452 (2002) 217.
[10] R.H. Wiedmeyer, T.W. May, Arch. Environ. Contam. Toxicol. 25 (1993) 67.
[11] T.W. May, D.A. Kane, Anal. Chim. Acta 161 (1984) 387.
[12] R. Sabe, R. Rubio, L. Garcia-Beltrán, Anal. Chim. Acta 436 (2001) 215.
[13] E. Vassileva, H. Docekalova, H. Baeten, S. Vanhentenrijk, M. Hoening, Talanta 54 (2001) 187.
[14] P. Bermejo-Barrera, A. Moreda-Pineiro, A. Bermejo-Barrera, Talanta 57 (2001) 969.
[15] P. Borella, A. Bargellini, E. Caselgrandi, A. Menditto, M. Patriarca, A. Taylos, G. Vivoli, Microchem. J. 58 (1998) 325.
[16] P. Bermejo, J.L. Capelo, A. Mota, Y. Madrid, C. Camara, Trac. Trends Anal. Chem. 23 (2004) 654.
[17] N. Gilon, A. Astruc, M. Astruc, M. Potin-Gautier, Appl. Organomet. Chem. 9 (1995) 623.
[18] Zs. Stefanka, I. Ipolyi, M. Dernovics, P. Fodor, Talanta 55 (2001) 437.
[19] E.T. Bodo, Z. Stefanka, I. Ipolyi, C. Soros, M. Dernovics, P. Fodor, Anal. Bioanal. Chem. 377 (2003) 32.
[20] J.L. Capelo-Martinez, P. Ximenez-Embun, Y. Madrid, C. Camara, Trac. Trends Anal. Chem. 23 (2004) 331.
[21] J.L. Gómez-Ariza, M.A.C. Torre, I. Giraldez, E. Morales, Anal. Chim. Acta 524 (2004) 305.
[22] H.C. Mehra, W.T. Frankenberger, Chromatographia 25 (1998) 585.
[23] M.G. Cobo-Fernández, M.A. Palacios, D. Chakraborti, P. Quevauviller, C. Camara, Fresenius J. Anal. Chem. 351 (1995) 438.
[24] R.J. Hrauss, S.J. Foster, H.E. Gauther, Anal. Biochem. 147 (1985) 432.
[25] R. Munoz, O. Donard, N. Gilon, M. Potin-Gautier, J. Anal. At. Spectrom. 12 (1996) 1171.
[26] P. Vinas, I. Lopez-Garcia, N. Campillo, M. Hernandez-Cordoba, Anal. Chim. Acta 535 (2005) 49.
[27] J.L. Gomez-Ariza, V. Bernal-Daza, M.J. Villegas-Portero, Anal. Chim. Acta 520 (2004) 229.
[28] J.M. Gonzalez, M.L. Fernández, A. Sanz-Medel, J. Anal. At. Spectrom. 11 (1996) 1163.
[29] N. Ellend, C. Rohrer, M. Grasserbauer, J.A.C. Broekaert, Fresenius J. Anal. Chem. 356 (1996) 99.
[30] D.L. Tsalev, L. Lampugnani, A. D'Ulivo, I.I. Petrov, R. Georgieva, K. Marcicci, R. Zamboni, Microchem. J. 70 (2001) 103.
[31] U. Sidenius, B. Gammelgaard, Fresenius J. Anal. Chem. 367 (2000) 96.
[32] B. Gammelgaard, E.H. Larsen, Talanta 47 (1998) 503.
[33] M.B.O. Giacomelli, M.C. Lima, V. Stupp, R.M.C. Junior, J.B.B. Silva, P. Bermejo-Barrera, Spectrochim. Acta 57B (2002) 2151.
[34] R.J. Hrauss, S.J. Foster, H.E. Gauther, Anal. Biochem. 147 (1985) 432.
[35] L. Schloske, H. Waldner, F. Marx, Anal. Bioanal. Chem. 372 (2002) 700.
[36] W. Goessler, K.J. Irgolic, Anal. Commun. 35 (1998) 361.
[37] M.E. Moreno, C. Pérrez-Conde, C. Cámara, Anal. Bioanal. Chem. 375 (2003) 666.
[38] J.L. Capelo, P. Ximenez-Embun, Y. Madrid-Albarran, C. Camara, Anal. Chem. 76 (2004) 233.
[39] L.H. Reyes, F.M. Sanz, P. Herrero Espilez, J.M. Marchante-Gayón, J.I.G. Alonso, A. Sanz-Medel, J. Anal. At. Spectrom. 19 (2004) 1230.
[40] A.I. Cabanero, Y. Madrid, C. Camara, Anal. Bioanal. Chem. 381 (2005) 373.
[41] F. Li, W. Goessler, K.J. Irgolic, Anal. Commun. 35 (1998) 361.
[42] R.R. Allabashi, J. Rendt, M. Grasserbauer, Fresenius J. Anal. Chem. 360 (1998) 723.
[43] U. Pyell, A. Dworschak, F. Nitschke, B. Neidhart, Fresenius J. Anal. Chem. 363 (1999) 495.
[44] A. Chatterjee, Y. Shibata, M. Morita, Microchem. J. 69 (2001) 179.
[45] F. Sahin, M. Volkan, A.G. Howard, O.Y. Ataman, Talanta 60 (2003) 1003.
[46] P. Cava-Montesinos, M. Luisa Cervera, A. Pastor, M. de la Guardia, Talanta 62 (2004) 175.
[47] H. Méndez, I. Lavilla, C. Bendicho, J. Anal. At. Spectrom. 19 (2004) 1379.