·专论与综述 ·

环境样品中铅、锑、汞、硒形态分析研究进展

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摘　要:综述了环境样品中铅、锑、汞、硒形态分析的研究进展,以及光谱法、色谱法、毛细管电泳及其联用技术在形态分析中的应用,展望了环境样品痕量元素形态分析的发展前景。

关键词:形态分析;铅;锑;汞;硒;环境样品

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Research Progress on Speciation Analysis of Lead, Antimony, Mercury and Selenium in Environmental Samples

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Abstract: A review on research progress of speciation analysis of lead, antimony, mercury and selenium in environmental samples was presented, with emphasis on the analytical applications of spectrometry, chromatography, capillary electrophoresis and hyphenated techniques. The prospect of trace element speciation analysis in environment field was also discussed.

Key words: Speciation analysis; Lead; Antimony; Mercury; Selenium; Environmental samples

铅(Pb)、锑(Sb)、汞(Hg)、硒(Se)是环境、生物和毒理学的重要元素,同一元素的不同化学形态,其毒性或生物可利用性有时差异很大。

铅是公认的蓄积性毒性元素[1]。有机铅污染来自广泛使用的汽油抗爆剂四烷基铅,在自然界水体中四烷基铅会降解成三烷基铅、二烷基铅,最后成为无机铅离子(一烷基铅极不稳定)。铅在人体中缓慢聚集到骨骼和软组织中,对健康造成危害,如慢性铅中毒可导致贫血、神经异常兴奋、脑损伤、肾功能失调等症状[2-3]。

在天然体系中,锑的各种氧化态(- Ⅲ、0、Ⅲ、Ⅴ)以无机、有机或胶体形式存在,在环境样品中,主要存在两种氧化态(Ⅲ、Ⅴ)。尽管锑元素很早就为人所知,但因其是公认的非生命必需元素,而且在环境中含量低(特别是在水环境中),因而长期以来未得到足够的关注[4]。然而,锑的毒性不容忽视,不同形态的锑化合物毒性不同,无机锑的毒性比有机锑大,摄入含锑物质会导致肺炎、骨髓损伤和癌症[5-6]。

汞是高毒元素,在生物和环境体系持久蓄积[7-8]。无机汞和甲基汞是环境和生物样品中主要存在的两种汞形态[8-9]。甲基汞是毒性最大的汞形体,高度稳定,易于穿透生物膜且通过食物链聚集[7,10]。由于具有亲脂性、生物累积效应和生物放大效应,甲基汞毒性是无机汞的几十倍。通过各种食物摄入的微量甲基汞进入人体后,可通过血脑屏障引起中枢神经系统永久性损伤[11]。无机汞在

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水生系统中可以通过生物和非生物甲基化作用转化为甲基汞化合物，从而增强毒性，直接对人类构成威胁。无机汞的甲基化过程是汞生物地球化学循环的一个重要环节。

硒为准金属，位于 ⅥA 族。自然界的硒来源于人类活动 (矿物燃料燃烧、工农业生产过程)和自然因素 (矿石风化)。环境样品中无机形态的硒主要有单质硒、硒的金属化合物、硒酸盐 SeO_4^{2-} 和亚硒酸盐 SeO_3^{2-}，有机硒主要有二甲基硒 (DMSe)、二甲基二硒 (DMDSe)和三甲基硒 (TMSe$^+$)等[12]。硒具有双重作用[13]，低浓度时是必需的营养元素，可形成含硒醇活性中心的谷胱甘肽过氧化物酶，保护细胞免于氧化损伤，过量则是有毒物质，无机硒的毒性大于有机硒[14]。

由于元素的作用及行为很大程度上取决于其化学形式和浓度，不同的形态产生不同的环境效应，直接影响到重金属的毒性、迁移及其在自然界中的循环[15]。因此，为获得元素在环境中的存在形式及迁移转化规律，不仅需要测定元素总量，而且需要测定元素的不同形态。

1 铅形态分析

环境水样中铅含量低微，预富集结合各种原子光谱技术是无机铅分析的主要手段，常用的富集手段包括沉淀、共沉淀、离子交换、溶剂萃取、固相萃取和浊点萃取等[1-3,16-21]。气相色谱与光谱、质谱技术联用是环境样品中有机铅形态分析的有力工具[22-33]。各种萃取技术在分离富集环境样品中痕量铅形态方面非常有效，特别是固相萃取 (SPE)[32-33]和固相微萃取 (SPME)[22-23,28-30]，操作简便快速，分离效果好，适用范围广，易与检测技术联用，实现在线分析。近年来环境样品中铅的形态分析方法见表 1[1-3,16-33]。

表 1 铅的形态分析方法

分析物	样品	方法①	检出限	文献
无机铅	天然水	HG - AAS	0.20 mg/L～0.85 mg/L	[1]
无机铅	饮用水和环境水样	HG - AFS	4 ng/L	[2]
无机铅	海水	ICP - OES	53 μg/L	[3]
无机铅	饮用水	HG - AFS	0.016 μg/L	[16]
无机铅	海水	ET - AAS	1.7 ng/L	[17]
无机铅	水样	FAAS	0.3 μg/L	[18]
无机铅	环境水样	FAAS	1.2 μg/L	[19]
无机铅	矿泉水和自来水	FAAS	2.4 μg/L	[20]
无机铅	水和废水	FAAS	1.5 μg/L	[21]
三甲基铅和三乙基铅	水	GC - MS	0.4 ng/L、0.2 ng/L	[22]
甲基铅和乙基铅	水样及其萃取物	GC - AES	0.2 ng/L	[23]
三乙基铅和无机铅	雨水	ICP - MS	90 ng/L～200 ng/L	[24]
铅同位素	四乙基铅	GC - ICP - MS	0.3 pg～20 pg	[25]
甲基铅和乙基铅	雨水	GC - MS、GC - AES、 GC - ICP - TOF - MS	15 fg(以 Pb计)	[26]
甲基铅和乙基铅	加标水样和标准参考物质 CRM 605	GC - ICP - TOF - MS	50 ng/L～75 ng/L	[27]
三甲基铅和三乙基铅	参考物底泥 PACS - 2	GC - OES	1.15 μg/L、0.03 μg/L	[28]
甲基铅和乙基铅	大气颗粒物	GC - ICP - MS	1.8 fg～9 fg	[29]
烷基铅和无机铅	水样	GC - MS、GC - FID	83 ng/L～130 ng/L	[30]
无机铅、甲基铅和乙基铅	环境水样	GC - MS	1 ng/L～4 ng/L	[31]
甲基铅和乙基铅	环境水样	GC - MS	4 ng/L～15 ng/L	[32]
无机铅、甲基铅和乙基铅	污水	GC - AAS	0.12 μg/L～0.30 μg/L	[33]

① HG - AAS指氢化物发生原子吸收光谱法；HG - AFS指氢化物发生原子荧光光谱法；ICP - OES指电感耦合等离子体原子发射光谱法；ET - AAS指电热原子吸收光谱法；FAAS指火焰原子吸收光谱法；GC - MS指气相色谱 - 质谱法；GC - AES指气相色谱 - 原子发射光谱法；ICP - MS指电感耦合等离子体质谱法；GC - ICP - MS指气相色谱 - 电感耦合等离子体质谱法；GC - ICP - TOF - MS指气相色谱 - 电感耦合等离子体飞行时间质谱法；GC - OES指气相色谱 - 原子发射光谱法；GC - FID指气相色谱 - 火焰离子化检测；GC - AAS指气相色谱 - 原子吸收光谱法。

2 锑形态分析

基于色谱和毛细管电泳分离方法的联用技术,可直接提供锑的形态信息。GC主要用于挥发性锑形体的分离[34], ICP-MS和飞行时间质谱(TOF-MS)是理想的检测手段;高效液相色谱(HPLC)可直接在室温下分离无机锑和有机锑,特别适用于环境样品和生物体液分析[35-44];毛细管电泳(CE)耦合 ICP-MS对于 Sb(Ⅲ)、Sb(Ⅴ)和 $(CH_3)_3SbCl_2$ 的成功分离显示了该技术在锑形态分析中的潜力[45]。对于难以完成联用技术仪器化的分析实验室来说,采用简单的非色谱方法,也是区分一二种锑形态行之有效的方法选择。主要的非色谱方法包括: ①分光光度法,成熟可靠,但灵敏度不高,近年来用于锑形态的报道较少[46]; ②X-射线精细结构光谱(XAFS),可直接提供固体样品中的形态信息,有助于了解污染土壤中锑的行为[47]; ③各种萃取技术结合原子光谱,可区分无机锑形态[48],特别是利用氢化物发生反应选择性地产生 SbH_3,是区分无机锑形体 Sb(Ⅲ)和 Sb(Ⅴ)最常用的方法。氢化物发生原子光谱法的非色谱分析方案主要基于 Sb(Ⅲ)和 Sb(Ⅴ)的选择性吸附[49]、配位剂抑制 Sb(Ⅴ)的氢化物发生反应[50-51]、Sb(Ⅲ)和 Sb(Ⅴ)的不同分析灵敏度[52]、酸度控制结合 Sb(Ⅴ)预还原[53]、Sb(Ⅲ)的光氧化[54]等。近年来环境样品中锑的形态分析方法见表 2。

表 2 锑的形态分析方法

分析物	样品	方法①	检出限	文献
Sb(Ⅲ)、Sb(Ⅴ)	土壤	HPLC-ICP-MS	20 ng/L、65 ng/L	[35]
Sb(Ⅲ)、Sb(Ⅴ)	环境水样	HPLC-ICP-MS	0.05 μg/L、0.07 μg/L	[36]
Sb(Ⅲ)、Sb(Ⅴ)、$(CH_3)_3SbCl_2$	合成水样	HPLC-ICP-MS		[37]
Sb(Ⅲ)、Sb(Ⅴ)、$(CH_3)_3SbCl_2$	自来水和河水	LC-HG-AFS	0.9 μg/L、0.5 μg/L、0.7 μg/L	[38]
$(CH_3)_3SbBr_2$、Sb(Ⅲ)、Sb(Ⅴ)	饮用水和地表水	HPLC-HG-AFS	0.04 μg/L、0.09 μg/L、0.26 μg/L	[39]
Sb(Ⅲ)、Sb(Ⅴ)、$(CH_3)_3SbCl_2$	河水	IC-HG-AFS	0.06 μg/L、0.09 μg/L、0.04 μg/L	[40]
Sb(Ⅲ)、Sb(Ⅴ)、$(CH_3)_3SbCl_2$	海水	HPLC-HG-AFS	0.13 μg/L、0.07 μg/L、0.13 μg/L	[41]
Sb(Ⅲ)、Sb(Ⅴ)、$(CH_3)_3SbCl_2$	自来水	HPLC-ICP-MS	14 ng/L、12 ng/L、9 ng/L	[42]
Sb(Ⅴ)、$(CH_3)_3SbCl_2$	空气颗粒物	HPLC-ICP-MS		[43]
Sb(Ⅲ)、Sb(Ⅴ)、$(CH_3)_3SbCl_2$	沉积物	HPLC-HG-AFS	30 ng/g	[44]
Sb(Ⅴ)、$(CH_3)_3SbCl_2$	污泥	CE-ICP-MS	0.1 mg/L～0.7 mg/L	[45]
Sb(Ⅴ)	土壤	XAFS		[47]
Sb(Ⅴ)	天然水	ICP-MS	0.7 ng/L	[48]
Sb(Ⅲ)、Sb(Ⅴ)、$(CH_3)_3SbCl_2$	水	HG-AFS	0.13 μg/L、0.07 μg/L、0.13 μg/L	[6]
Sb(Ⅲ)、Sb(Ⅴ)	天然水	HG-AFS	2.3 ng/L	[49]
Sb(Ⅲ)	湖水	HG-AFS	10 ng/L	[50]
Sb(Ⅲ)、Sb(Ⅴ)	土壤	HG-AFS	17 ng/L、10 ng/L	[51]
Sb(Ⅲ)、Sb(Ⅴ)	水样	HG-ICP-AES	1.2 μg/L、4.5 μg/L	[52]
Sb(Ⅲ)、Sb(Ⅴ)	天然水	HG-AFS	6 ng/L～14 ng/L	[53]
Sb(Ⅲ)、Sb(Ⅴ)	海水	HG-AFS	5 ng/L、10 ng/L	[54]
Sb(Ⅲ)	海水	HG-ICP-OES	0.043 μg/L	[55]
Sb(Ⅲ)	天然水和土壤	ETAAS	0.3 μg/L	[56]
Sb(Ⅲ)、Sb(Ⅴ)	自来水	HG-AAS	7 ng/L	[57]

① LC-HG-AFS指液相色谱-氢化物发生原子荧光光谱法; IC-HG-AFS指离子色谱-氢化物发生原子荧光光谱法; HG-ICP-AES指氢化物发生-电感耦合等离子体原子发射光谱法。

3 汞形态分析

分离方法与元素选择性检测器在线耦合是汞形态分析的发展趋势, GC[58-60]、HPLC[61-63]、IC[64]和 CE[65]等各种分离方法联用技术已用于汞形态分析。在环境和生物样品中,汞含量很低,分离检测前的样品预富集十分必要,采用的富集手段主要有固相微萃取[66]、液-液萃取[67]、固相萃取[68-70]、浊点萃取[71]、Tenax管捕集[72]和冷肼捕集[73]。利用简单的非色谱方法可区分一二种汞形体(如无机汞和甲基汞),其中冷蒸气原子吸收光

谱法 (CV - AAS)[74 - 78]和冷蒸气原子荧光光谱法 (CV - AFS)[79 - 81]最为常用。CV - AAS区分汞形态的分析方案[74,76,81]主要基于还原剂的不同选择性、$NaBH_4$浓度差别和石英原子化器温度差异; CV - AFS[79 - 81]则基于选择性富集、在线氧化分解、紫外辐射和光化学诱导等手段区分汞形态。近年来环境样品中汞的形态分析方法见表 3。

表 3 汞的形态分析方法

分析物	样品	方法①	检出限	文献
无机汞、甲基汞	水环境样品	GC - ICP - MS	15 pg、3 pg	[59]
无机汞、甲基汞	雪	GC - ICP - TOF - MS	150 pg/L、2 pg/L	[60]
无机汞、甲基汞	天然淡水	HPLC - UV - CV /HG - AFS	11 μg/L、8 μg/L	[62]
甲基汞、无机汞	土壤	HPLC - ICP - MS	15 ng/L	[63]
无机汞、甲基汞	冰和环境标准物质	GC - ICP - TOF - MS	0. 27 pg/g、0. 027 pg/g	[66]
无机汞、甲基汞	天然水	GC - CV - AFS	0. 06 ng/L、0. 006 ng/L	[67]
无机汞和有机汞 (甲基汞、乙基汞和苯基汞)	海水和废水	HPLC - UV	10 ng/g～25 ng/g	[69]
无机汞和有机汞 (甲基汞和乙基汞)	水	GC - MS	1. 5 ng/L	[70]
无机汞、总汞	沉积物	CV - AAS	3. 9 ng/L、24 ng/L	[74]
无机汞、甲基汞	海底沉积物	CV - AAS	10 ng/L、18 ng/L	[75]
无机汞、甲基汞	饮用水、海水	CV - AAS	40 ng/L、80 ng/L	[76]
无机汞、总汞	水	CV - AAS	14 ng/L、14 ng/L	[77]
甲基汞、无机汞	水	CV - AAS	0. 96 ng/L、0. 25 ng/L	[78]
无机汞、甲基汞	河水	CV - AFS	0. 07 ng/L、0. 05 ng/L	[79]
无机汞、总汞	水	CV - AFS	200 μg/L、3 μg/L	[80]
无机汞、甲基汞	水	CV - AFS	3. 6 ng/L、2. 0 ng/L	[81]

① HPLC - UV - CV /HG - AFS指高效液相色谱 - 紫外辐射氧化 - 冷蒸气 /氢化物发生原子荧光光谱法。

4 硒形态分析

环境中的硒常与硫共存,硒的地壳丰度不高,仅为 0. 05 μg/g～0. 09 μg/g,天然水中总硒质量浓度为 0. 1 μg/L～400 μg/L,大气中约 1 ng/L,土壤中质量比为 0 μg/g～80 μg/g[82]。环境样品硒的形态一直是研究的热点方向,已有多篇综述报道[12,82 - 84]。HPLC[85 - 88]、阴离子交换色谱 (AEC)[89]、IC[90 - 91]、CE[92 - 94]等分离手段与光谱、质谱技术联用可直接提供硒的形态信息,是形态分析的发展方向。非色谱分析方法简单易行,广泛用于环境样品中一二种无机硒的形态分析,主要方法包括: ①选择性富集结合各种光谱分析方法,如 ICP - MS、ET - AAS、石墨炉原子吸收光谱法 (GF - AAS)、HG - AFS、能量分散 X -射线荧光光谱法等[95 - 99]; ②HG - AAS[100]或 AFS[101]直接测定 Se(Ⅳ),总无机硒 [Se(Ⅳ) + Se(Ⅵ)]预还原测得总量,差减求得 Se(Ⅵ); ③动力学光度法测定 Se(Ⅳ), Se(Ⅵ)预还原测得总量[102]。近年来环境样品中硒的形态分析方法见表 4。

表 4 硒的形态分析方法

分析物	样品	方法①	检出限	文献
Se(Ⅳ)、Se(Ⅵ)	雨水和加料水	HPLC - ICP - MS	0. 07 μg/L～0. 18 μg/L	[85]
Se(Ⅳ)、Se(Ⅵ)	沉积物	HPLC - ICP - MS	0. 9 μg/L、1. 2 μg/L	[86]
Se(Ⅳ)、Se(Ⅵ)	自来水和海水	HPLC - HG - AFS	0. 2 μg/L、0. 5 μg/L	[87]
Se(Ⅳ)、Se(Ⅵ)	海水和雨水	AEC - HG - ICP - MS	0. 15 ng/L、0. 27 ng/L	[89]
Se(Ⅳ)、Se(Ⅵ)	工业废水	IC - ICP - MS	1 μg/L	[90]
Se(Ⅳ)、Se(Ⅵ)	土壤	CE - CD	190 μg/L、7. 5 μg/L	[92]
Se(Ⅳ)、Se(Ⅵ)	加料天然水	CE - HG - AFS	33 μg/L、25 μg/L	[93]
Se(Ⅳ)、Se(Ⅵ)	水	ICP - MS	7 ng/L	[95]
Se(Ⅳ)、Se(Ⅵ)	自来水	ET - AAS	0. 01 μg/L	[96]

续表

分析物	样品	方法①	检出限	文献
Se(Ⅳ)、Se(Ⅵ)	天然水和污泥	GF - AAS	4.7 ng/L、6.3 ng/L	[97]
Se(Ⅳ)、Se(Ⅵ)	天然水	HG - AFS	0.014 μg/L	[98]
Se(Ⅳ)、Se(Ⅵ)	合成水样	能量分散 X - 射线荧光光谱法	60 μg/L	[99]
Se(Ⅳ)、Se(Ⅵ)	水样和橙汁	HG - AAS	0.25 μg/L、0.30 μg/L	[100]
Se(Ⅳ)、Se(Ⅵ)	环境水样	动力学光度法	1.3 μg/L	[102]

① CE - CD指毛细管电泳电导法。

5 结语

近年来在环境样品 Pb、Sb、Hg、Se的形态分析方面取得了较大进展，色谱、毛细管电泳、微流控芯片等分离技术与光谱、质谱分析技术联用是元素形态分析的发展方向，非色谱分析方法简单、经济，是一般实验室区分同一元素几种主要形态的有效手段。环境样品中元素各种形态含量甚微，样品基体复杂，今后的研究方向仍将是建立先进的分离富集前处理方法和发展高灵敏、高选择性的检测技术，在此基础上，进一步提高联用技术水平，实现环境样品痕量元素形态的现场实时分析。

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·简讯 ·

11项国家排放新标准全面提升污染控制水平

环境保护部日前颁布的 11项排放标准,分别为:《制浆造纸工业水污染物排放标准》《电镀污染物排放标准》《羽绒工业水污染物排放标准》《合成革与人造革工业污染物排放标准》《发酵类制药工业水污染物排放标准》《化学合成类制药工业水污染物排放标准》《提取类制药工业水污染物排放标准》《中药类制药工业水污染物排放标准》《生物工程类制药工业水污染物排放标准》《混装制剂类制药工业水污染物排放标准》《制糖工业水污染物排放标准》。

这些标准按照新时期国家环境保护执法和监管工作的要求、结合具体适用行业生产工艺和污染治理技术的特点设置,标准对现有企业和建设项目分别提出了污染物排放控制要求(建设项目 2008年 8月 1日起实施),并且规定经过一个过渡期后,现有企业要达到与建设项目相同的排放控制要求。这 11项标准在选择确定控制排放的污染物项目方面充分体现了行业排放标准的特点和要求,既包括化学需氧量、pH值、总悬浮物、生化需氧量、氨氮、总氮、总磷、氮氧化物、颗粒物等水气常规污染物,又有行业特有的有毒污染物(如二恶英、重金属、氰化氢、铬酸雾、苯系物等)项目。制药工业 6项排放标准还规定了采用发光细菌法检测的生物综合毒性指标。此外,还规定了各类污染物的监控位置、测定方法、排放浓度核算方法、超标排放判定方法、排入城市污水处理厂污水监控方式等内容。

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