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快速连续提取沉积物中还原性无机硫的实验方法与应用

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摘要: 还原性无机硫是沉积物硫中最活跃的部分,其含量变化控制沉积物中铁、磷及重金属等元素的地球化学行为,在地质过程和环境污染方面都具有至关重要的影响。化学连续提取法是目前沉积物中硫形态提取基本方法,但常用的冷扩散法处理单个样品耗时长,难以实现对大批量样品的快速连续提取。为实现快速、准确地测定沉积物样品各形态还原性无机硫的含量,本文采用热蒸馏法,改进基于前人的三步提取过程,通过优化实验装置预先制备实验所需的二氯化铬溶液,实现了样品还原性无机硫形态的快速连续提取;以过氧化氢为氧化剂,将提取的各形态硫氧化为 SO_4^{2-} 后采用离子色谱进行检测。选取三峡库区沉积物样品进行重复实验检验,得到提取酸挥发性硫、黄铁矿硫、元素硫的标准偏差(RSD, $n=3$)分别为 5.26%、1.22%和 3.09%,重复性较好。进一步对酸挥发性硫、黄铁矿硫、元素硫的加标回收率进行测定,得到这三种硫形态的回收率分别为 92.8%、93.6%、94.1%。本实验方法采用的热蒸馏法对单个硫形态提取时间为 1.5h,用时较短,玻璃装置连接便捷、操作简单,分析检测准确度好,实现了一套装置对沉积物还原性无机硫形态的连续提取,可适用于大批量样品的硫形态快速提取与检测。

关键词: 还原性无机硫; 热蒸馏法; 硫形态提取; 沉积物; 离子色谱法

要点:

(1) 所设计的实验装置实现了对各形态还原性无机硫的连续提取。

(2) 提取出的各形态还原性无机硫采用过氧化氢氧化为 SO_4^{2-} 后,实现了离子色谱的统一检测。

(3) 三峡库区沉积物的研究显示,库区硫污染程度较低。

中图分类号: O637.31　　**文献标识码:** A

硫(S)是水生生态系统中最重要的生源要素之一,影响生态系统的结构、功能和生产力。硫元素在参与植物氨基酸、叶绿素的合成以及光合作用中的碳水化合物代谢、植物呼吸等过程中发挥重要的作用[1-4]。水体沉积物中硫的化学价态多变(从-2 到+6 价),按照其存在形态分为无机硫和有机硫两类[5]。已有研究表明无机硫可占植物硫吸收总量的 55%以上[6]。无机硫主要包括:酸挥发性硫化物(AVS)、黄铁矿硫(CRS)和元素硫(ES),这些都为还原性无机硫。还原性无机硫也是沉积物中硫形态最活跃的部分,不仅影响植物的生长,还对沉积物中的铁、磷及重金属的地球化学行为起到了控制性的作用[7-8]。此外,酸挥发性硫化物分析还被越来越多地应用到沉积物重金属的生物毒性评价中[9-10]。因为 S^{2-} 能够与绝大多数重金属离子相结合,形成不易被生物利用的难溶性硫化物,从而降低了沉积物中重金属的化学活性和生物有效性,对于控制沉积物重金属生物毒性和生态风险能起到关键作用[11]。

为研究不同形态还原性无机硫的环境行为和生物有效性,沉积物中硫形态的提取和分析方法也在

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不断地发展和完善。Nriagu 等[12]在 1985 年提出的硫形态连续提取原理为后期研究硫形态奠定了基础。目前,硫形态的提取过程主要采用热蒸馏装置和冷扩散装置[9,13-14]。热蒸馏装置方法为:将沉积物样品加热至混合试剂的沸点与盐酸反应,通过氮气将生成的硫化氢气体(H_2S)吹脱至吸收液中。而冷扩散装置法是在热蒸馏法基础上简化的一种提取方法,主要是将装有吸收液的瓶子放入密闭的反应装置中,通过装置中气体浓度差异将生成的硫化氢气体不断地扩散至吸收液中完全吸收[15]。冷扩散法与热蒸馏法相比,虽然装置较为简单,但单一样品的反应一般需要 24h,而热蒸馏法提取单个形态时间一般只需 1.5h,能极大地提高提取效率。在硫形态提取过程中生成的硫化氢气体一般采用乙酸锌溶液吸收,使用亚甲基蓝法(比色法)[16]、碘量法等方法检测[17]。但这些方法存在测试过程繁琐、分析时间长、硫成分易损失等缺点。随着现代分析仪器的发展和普及,电感耦合等离子体质谱法(ICP-MS)、离子色谱法等因其分析快速、准确率高、检测限低等优势,被越来越多地应用到硫形态检测中[18-22]。

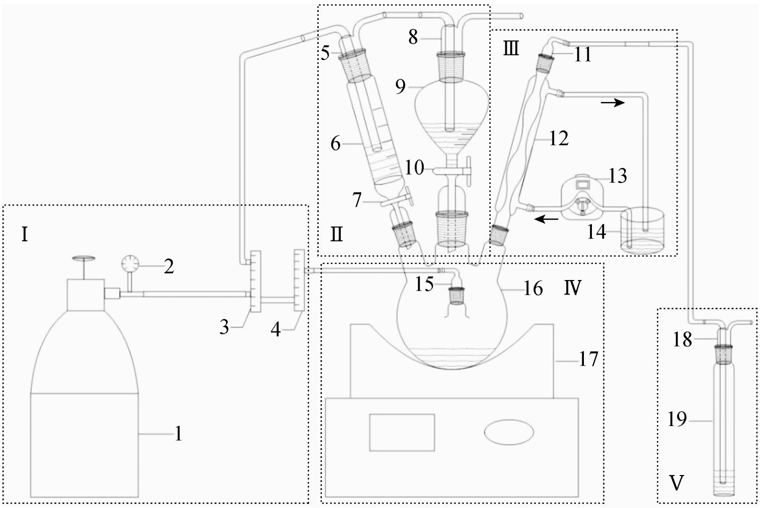
国内外目前对于沉积物中还原性无机硫的提取多采用冷扩散法,但存在难以适应地质、环境研究中样品数量多、样品长时间保存不便等情况。本文研制了一套沉积物中还原性无机硫的快速提取装置及分析方法,即:采用耗时短的热蒸馏法连续提取沉积物中的还原性无机硫,将其转化为硫化氢气体后,经氢氧化钠溶液吸收、加入过氧化氢(H_2O_2)氧化为 SO_4^{2-} 后使用离子色谱进行检测。为进一步验证本实验装置的可靠性和实际应用价值,本文还选取了长江三峡库区沉积物样品进行了还原性无机硫的提取分析,研究结果可为三峡库区的水环境治理提供有益的参考。

1　还原性无机硫提取装置的研制

1.1　装置组成

本实验基于前人沉积物中还原性无机硫的三步提取方法和装置[13,23],设计了新的实验装置如图 1 所示。装置由五个部分组成,分别为:氮气源(Ⅰ)、加液系统(Ⅱ)、冷凝系统(Ⅲ)、反应系统(Ⅳ)和吸收系统(Ⅴ),且所有连通部位均以透明硅胶管作为连接器来进行封闭式连通。

装置五个部分具体连通流程为:首先,将氮气减压阀 2、第一气体流量计 3、第二气体流量计 4 连接;然后将层析柱玻璃弯头 5 和第一气体流量计 3、分液漏斗玻璃弯头 8 连接,将第二气体流量计 4、四口



实验装置部件包含: 1—氮气瓶; 2—减压阀; 3—第一气体流量计; 4—第二气体流量计; 5—层析柱玻璃弯头; 6—层析柱; 7—层析柱阀门; 8—分液漏斗玻璃弯头; 9—分液漏斗; 10—分液漏斗阀门; 11—冷凝管玻璃弯头; 12—冷凝管; 13—蠕动泵; 14—烧杯; 15—烧瓶玻璃弯头; 16—四口烧瓶(反应器); 17—加热装置; 18—试管玻璃弯头; 19—玻璃试管。

图 1　沉积物还原性无机硫连续提取装置

Fig. 1　The device for continuous extracting the reduced inorganic sulfur from sediments, including: 1—nitrogen cylinder, 2—pressure reducing valve, 3—the first gas flowmeter, 4—the second gas flowmeter, 5—glass elbow, 6—chromatography column, 7—valve of chromatography column, 8—glass elbow of dispenser funnel, 9—dispenser funnel, 10—valve of dispenser funnel, 11—glass elbow of condenser tube, 12—condenser tube, 13—peristaltic pump, 14—beaker, 15—glass elbow of flask, 16—four-mouth flask (reactor), 17—heating mantle, 18—glass elbow of tube , 19—glass tube.

烧瓶、层析柱 6、分液漏斗 9、冷凝管 12 相连；再次，将冷凝管 12 下方出口与蠕动泵 13 左侧接口连接，蠕动泵 13 右侧接口通过连接管插入烧杯 14 中，冷凝管 12 上方出口的连接管置于烧杯 14 中；最后将冷凝管玻璃弯头 11 与玻璃试管弯头 18 相连。

1.2　实验原理与装置性能特点

本实验采用热蒸馏法连续提取沉积物中的还原性无机硫，将其转化为硫化氢气体，经氢氧化钠溶液吸收，用过氧化氢氧化为 SO_4^{2-} 后通过离子色谱检测。所设计的提取装置密封性好、操作简单，可实现不同形态还原性无机硫的连续提取，分析检测便捷。装置通过试管玻璃弯头与玻璃试管连接，易于取出更换，可提高更换样品的速度，适用于样品数量较多的地质、环境调查分析。

2　实验部分

2.1　实验样品采集及特征

长江三峡库区沉积物样品为 2017 年 8 月和 2017 年 12 月采集的三峡库区云阳至秭归段 8 个长江干流点位样品（云阳上、云阳下、故陵镇、曲尺乡、巫山县、绿竹筏村、屈原镇、秭归），共 16 件。采样使用船载采样器采集水界面下表层 5cm 深的沉积物，样品用聚乙烯自封袋盛装，低温冷藏保存。返回实验室后，将沉积物样品真空冷冻干燥后（−4℃），于 4℃低温密封保存，并及时进行还原性无机硫的提取分析。

2.2　测试仪器

实验过程中，水溶液的离子测试分析在河海大学地球科学与工程学院使用 ThermoFisher Scientific 公司 Aquion 型离子色谱仪进行，仪器流量准确度优于 0.1%，流量精确度为±0.1%，检测器分辨率为 0.00238nS/cm，测试误差<5%。

2.3　实验方法

提取沉积物中的还原性无机硫的具体实验流程如图 2 所示。为实现连续提取酸挥发性硫、黄铁矿硫、元素硫目的，本装置设计了预先制备提取黄铁矿硫、元素硫所需的二氯化铬溶液（$CrCl_2$）的实验步骤。

2.3.1　二氯化铬溶液制备及实验准备

关闭图 1 所示的分液漏斗阀门 10，在分液漏斗 9 中加入 6mol/L 盐酸 30mL。因为提取还原性无机硫使用的盐酸需经过氮气吹脱，所以在此预先设置了和制备二氯化铬溶液一起使用氮气吹脱盐酸的过程。

以 1mol/L 稀盐酸为溶剂配制 1mol/L 三氯化铬

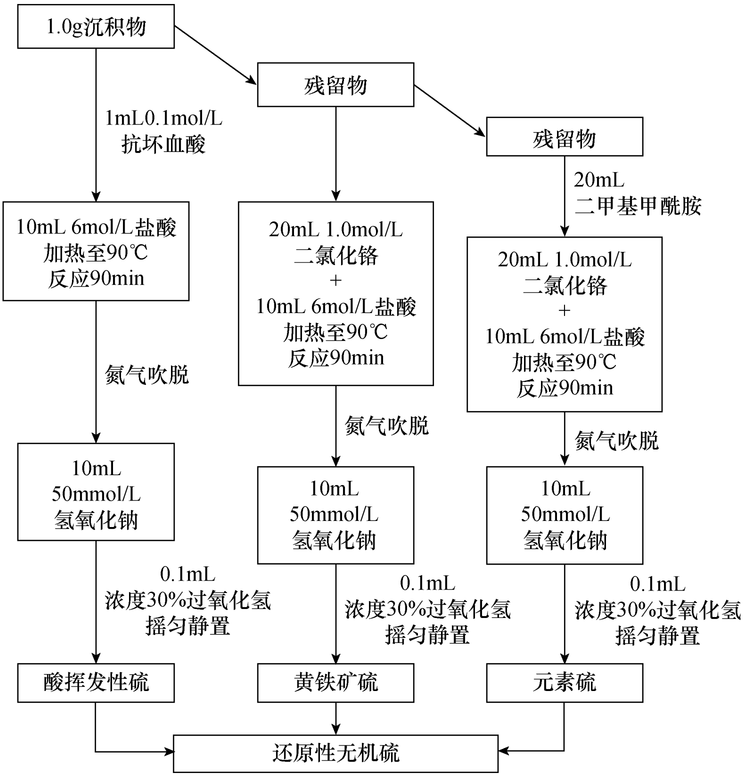


图 2　连续提取沉积物中还原性无机硫流程图

Fig. 2　Schematic diagram of continuously extracting the reduced inorganic sulfur from sediments.

溶液（$CrCl_3$）。关闭层析柱阀门 7,将 120g 锌粒和配制好的 40mL 三氯化铬溶液加入层析柱 6 中。依次打开图 1 所示的氮气瓶 1、减压阀 2、第一气体流量计 3、第二气体流量计 4,调节氮气流速以 20mL/min 的速率对反应装置和盐酸通氮气 20min,使氮气通过整个装置,检查装置密闭性；在还原环境、酸性条件下通过金属锌将三氯化铬溶液还原得到二氯化铬溶液,该过程包括两个反应方程式：

$$Zn(s)+2HCl(aq)=ZnCl_2(aq)+H_2(g) \tag{1}$$

$$2CrCl_3(aq)+Zn(s)=2CrCl_2(aq)+ZnCl_2(aq) \tag{2}$$

当层析柱 6 中溶液颜色由绿色变成亮蓝色时,二氯化铬溶液即制备完成。打开蠕动泵 13,保持冷凝管 12 持续工作。至此,硫形态提取实验准备工作结束。

2.3.2　还原性无机硫形态的提取及测定

（1）酸挥发性硫（AVS）

酸挥发性硫主要是二价金属（Cu、Ni、Pb、Zn 等）硫化物。加入盐酸后,金属硫化物会与其反应生成硫化氢气体,如 $CuS+2HCl=H_2S+CuCl_2$。硫化氢气体进入氢氧化钠溶液后会发生以下反应：$2NaOH+H_2S=Na_2S+2H_2O$。而后加入双氧水,可以将-2 价的硫氧化为+6 价：$Na_2S+4H_2O_2=Na_2SO_4+4H_2O$。最后通过离子色谱测定溶液中 SO_4^{2-} 浓度换算得到酸挥发性硫的含量。具体提取步骤如下。

取 1.00g 沉积物样品加入四口烧瓶 16 中,加入图 1 所示的磁子和 0.1mol/L 抗坏血酸 1mL,往玻璃试管 19 中加入 10mL 浓度为 50mmol/L 氢氧化钠吸收液,调节氮气速率为 20mL/min,除去反应系统和吸收系统中的空气后打开分液漏斗阀门 10,根据分液漏斗的刻度标识加入 10mL 盐酸到四口烧瓶 16 中。打开数显搅拌电热套 17,加热至 90℃,调节氮气速率以约 5～10mL/min 的流速将生成的硫化氢气体缓慢吹脱至玻璃试管 19 中,反应 90min。然后调节氮气流速至 20mL/min 继续吹脱 20min,下一步取出装有溶液的玻璃试管 19,加入 0.1mL 过氧化氢（浓度为 30%）摇匀静置 10min 后待检测。同时快速放入另一个含有 10mL 氢氧化钠溶液（50 mmol/L）的玻璃试管为下一步提取黄铁矿硫作准备,连接好玻璃弯头 18 后通氮气 30s。

（2）黄铁矿硫（铬还原性硫, CRS）

黄铁矿硫主要化学成分为二硫化亚铁（FeS_2）,在酸性条件下通过 Cr^{2+}将二硫化亚铁转化为硫化氢气体,反应原理为：$4H^+ +2Cr^{2+} +FeS_2 \rightarrow 2H_2S+2Cr^{3+} + Fe^{2+}$。产生的硫化氢气体进入氢氧化钠溶液后加入双氧水,将-2 价的硫氧化为+6 价 SO_4^{2-}。通过离子色谱测定 SO_4^{2-} 浓度并换算得到黄铁矿硫的含量。具体提取步骤如下。

在提取酸挥发性硫步骤完成后,打开图 1 所示的层析柱阀门 7,根据层析柱刻度指示加入 20mL 二氯化铬溶液（在 2.3.1 节中已加入层析柱中）,打开分液漏斗阀门 10,根据分液漏斗的刻度标识加入 10mL 盐酸到四口烧瓶 16 中,打开数显搅拌电热套 17,加热至 90℃,以 5～10mL/min 的氮气流速将生成的硫化氢气体缓慢吹脱至玻璃试管 19 中,反应 90min 后调节氮气流速至 20mL/min 继续吹脱 20min。然后取出装有氢氧化钠溶液的玻璃试管 19,加入 0.1mL 过氧化氢（浓度为 30%）摇匀静置 10min；同时快速放入另一个含有 10mL 氢氧化钠溶液（50mmol/L）的玻璃试管为下一步提取元素硫作准备,连接好玻璃弯头 18 后通氮气 30s。

（3）元素硫（ES）

元素硫主要是中间态的零价硫,难溶于水,但与有机溶剂结合能力较强,因此加入 DMF（N,N-二甲基甲酰胺）萃取。在酸性条件下通过 Cr^{2+}将零价硫转化为硫化氢气体,反应原理为：$2H^+ +2Cr^{2+} +S^0 \rightarrow H_2S+2Cr^{3+}$。产生的硫化氢气体进入氢氧化钠溶液后加入过氧化氢,将-2 价的硫氧化为+6 价 SO_4^{2-},再通过离子色谱测定 SO_4^{2-} 浓度,从而换算得到元素硫的含量。具体提取步骤如下。

在提取黄铁矿硫步骤完成后,通过图 1 所示的玻璃弯头 15 往反应器 16 中加入 20mL 二甲基甲酰胺,由于其对塑料有溶解作用,所以不能从三通阀处直接注入,连接好装置后通氮气 30s；打开层析柱阀门 7 和分液漏斗阀门 10,分别从层析柱、分液漏斗加入 20mL 二氯化铬溶液和 6mol/L 盐酸 10mL,打开数显搅拌电热套 17,加热至 90℃,以 5～10 mL/min 的氮气流速将生成的硫化氢气体缓慢吹脱至玻璃试管 19 中,反应 90min 后调节氮气流速至 20mL/min 继续吹脱 20min。取出装有氢氧化钠溶液的玻璃试管 19,加入 0.1mL 过氧化氢（浓度为 30%）,摇匀静置 10min 后溶液待检测。

3　实验方法的精密度和准确度

为对本研究改进的热蒸馏法提取还原性无机硫实验方法的准确度和精密度进行验证,进一步开展了重复性和加标对比实验（表 1）。选取沉积物样品

表 1　重复实验与加标实验结果

Table 1　Results of repeated experiment and spike recovery in AVS, CRS, and ES procedures.

硫形态	重复实验					加标实验(回收率)				
	第一次实验(μmol/g)	第二次实验(μmol/g)	第三次实验(μmol/g)	平均值(μmol/g)	RSD(%)	第一次实验(%)	第二次实验(%)	第三次实验(%)	平均值(%)	RSD(%)
酸挥发性硫(AVS)	0.20	0.19	0.18	0.19	5.26	91.6	93.2	93.6	92.8	1.14
黄铁矿硫(CRS)	3.13	3.06	3.12	3.10	1.22	93.4	95.7	91.7	93.6	2.14
元素硫(ES)	0.38	0.38	0.36	0.37	3.09	94.6	93.8	93.9	94.1	0.46

(三峡秭归,冬季)开展重复性实验 3 次($n=3$),得到酸挥发性硫、黄铁矿硫、元素硫的平均值分别为 0.19、3.10、0.37μmol/g,实验结果的相对标准偏差(RSD)分别为 5.26%、1.22%和 3.09%,重复性较优。进一步分别用 1mmol/L 九水硫化钠($Na_2S \cdot 9H_2O$)、黄铁矿(GBW07267)、高纯硫对酸挥发性硫、黄铁矿硫、元素硫的回收率进行测定,实验结果显示这三种硫形态的回收率分别为 92.8%、93.6%、94.1%,实验结果的相对标准偏差(RSD)分别为 1.14%、2.14%和 0.46%,加标回收率较理想。

李肖等[24]采用改进的“冷扩散法”测定沉积物中还原态无机硫含量,实验过程中通过 90℃水浴加热将“冷扩散法”提取酸挥发性硫、黄铁矿硫和元素硫的提取反应时间分别缩短为 1.5h、2h 和 2h;其在实验中加入固体硫化锌(ZnS)进行酸挥发性硫的回收实验,回收率为 82.01%~108.71%。王小芳等[25]与李肖等[24]采用相同提取方法通过配制标准溶液作为提取剂的方式进行沉积物元素硫的回收实验,回收率为 92.25%~98.08%($n=3$)。通过以上其他实验对比可以看出,本研究实验的加标回收率相对较优。本文的热蒸馏法沉积物还原性无机硫提取装置和实验方法的分析准确度较高,精密度也较好。

4　讨论

4.1　实验的操作效率分析

多数沉积物样品赋存于缺氧的沉积环境中,这些新鲜的沉积物样品必须及时处理,减少硫化物再氧化的风险[15],快速、准确也是相关行业对大批量样品硫含量分析测试的基本要求[22]。本实验所采用的热蒸馏法相比冷扩散法能较大地缩短实验时间。由于冷扩散法装置简单、易操作,传统的硫形态多采用冷扩散法提取[23]、亚甲基蓝法[16,26]或碘量法[17]检测,其中酸挥发性硫、元素硫的提取需要 18~24h,黄铁矿硫则需 48h,反应时间较长[27-28]。而本实验系统采用的热蒸馏法对单个形态提取为 1.5h,完成 3 种形态的提取时间大约需要 4.5h 时,时间大大缩短,已有研究表明加热可有效地缩短硫形态的提取时间[29]。

所设计的试验装置操作简便,装置采用试管玻璃弯头与玻璃试管连接,易于取出更换,可实现沉积物中各形态还原性无机硫的连续提取,能有效地提高热蒸馏法的实验效率。同时,根据研究者自身需要,还可以增加提取组数,通过多通器件与氮气瓶连接,进一步实现多组样品的同时处理。过氧化氢可以短时间将硫化氢氧化成硫酸盐[12]。本实验方法选取过氧化氢作为氧化剂,将各形态实验提取出的硫化氢采用氢氧化钠溶液吸收后氧化为 SO_4^{2-},再通过离子色谱测定 SO_4^{2-} 浓度,并换算得到各形态硫的含量。由于过氧化氢在常温下是液态,可以直接将硫化氢的输送管插入含有过氧化氢的溶液内。采用过氧化氢不仅可以快速地氧化硫化氢,其产物 SO_4^{2-} 还可以实现使用离子色谱进行检测,检测方法简单可靠,仪器检测的准确度高。

4.2　三峡库区沉积物测试分析

4.2.1　三峡库区沉积物还原性无机硫特征

采用本研究的实验装置和方法进行了三峡库区表层沉积物样品还原性无机硫的测定。实验所用样品为 2017 年 8 月和 12 月分别于三峡库区云阳至秭归段 8 个长江干流点位采集的沉积物(图 3),三峡库区表层沉积物中还原性无机硫的平均含量及组成情况见表 2。

表 2　三峡沉积物与太湖表层沉积物还原性无机硫的含量

Table 2　Composition of AVS, CRS, and ES in sediments of the Three Gorges Reservoir area and Taihu Lake.

采样地区	酸挥发性硫(μmol/g)	元素硫(μmol/g)	黄铁矿硫(μmol/g)
三峡库区平均值(本研究,$n=16$)	0.22	0.50	4.37
太湖梅梁湾北部[30]	1.00	2.70	10.20
太湖西五里湖[30]	1.90	0.60	10.30

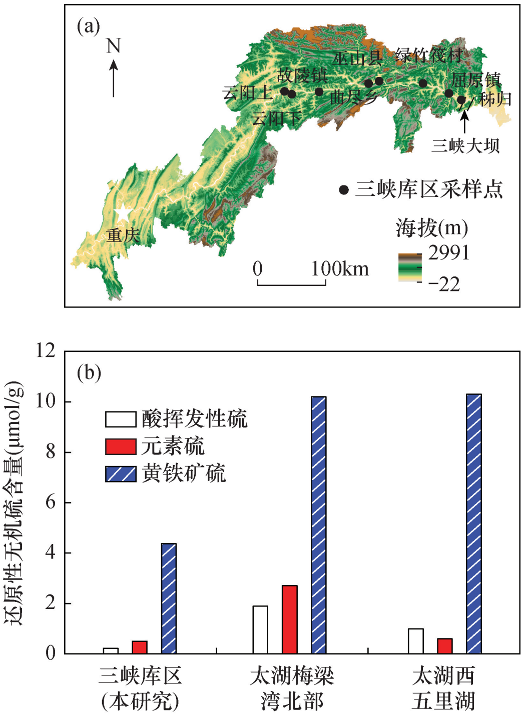


图 3　(a) 三峡库区采样点分布；(b) 三峡沉积物与太湖表层沉积物还原性无机硫含量对比[30]

Fig. 3　(a) Sampling points in the Three Gorges Reservoir area; (b) Comparison of AVS, CRS, and ES in sediments of the Three Gorges Reservoir area and Taihu Lake. Taihu Lake data are taken from Yin, et al. (2008)[30].

表 2 结果显示测得三峡沉积物样品的酸挥发性硫、元素硫和黄铁矿硫的平均含量分别为 0.22、0.50 和 4.37μmol/g。尹洪斌等[30]采用改进的冷扩散法测试了长江下游太湖北部沉积物还原性无机硫的含量，其样品采集于富营养化污染较为严重的太湖梅梁湾北部与西五里湖。进一步分析可知，本研究的三峡库区沉积物酸挥发性硫、黄铁矿硫和元素硫的平均含量均略低于太湖北部研究结果(表 2，图 3)。三峡库区的酸挥发性硫含量相对较低，未达到污染的程度，有学者指出未受污染的湖泊沉积物中酸挥发性硫含量范围为 4~13μmol/g[31]。由于太湖是富营养化型湖泊，有机质含量较高，加快了硫酸盐的还原过程，在极端厌氧的水环境中酸挥发性硫很难与沉积物中的元素硫发生氧化反应，从而导致了积累[32]。

4.2.2　三峡库区还原性无机硫的季节性变化

三峡库区夏季与冬季表层沉积物中还原性无机

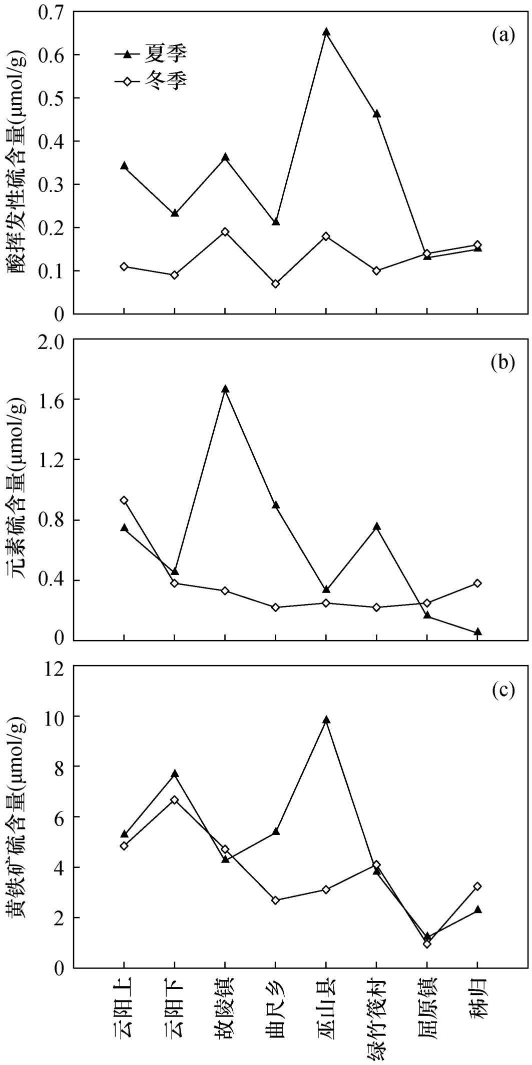


图 4　三峡库区沉积物还原性无机硫形态季节性组成特征(a 酸挥发性硫，b 元素硫，c 黄铁矿硫)

Fig. 4　Spatial and seasonal distribution characteristics of RIS in surface sediments of the Three Gorges Reservoir area, (a) acid volatile sulfur, (b) elemental sulfur, (c) pyrite sulfur.

硫(RIS)组成均以黄铁矿硫为主，占 68%~93%(图 4)。三峡库区干流沉积物中 RIS 含量呈现明显的季节性变化。总体上，三峡库区表层沉积物中 RIS 各组分含量从高到低为：黄铁矿硫>元素硫>酸挥发性硫。夏季酸挥发性硫平均含量为 0.32μmol/g，冬季为 0.13μmol/g，冬季酸挥发性硫含量只有夏季的 41%左右，表现为夏季高于冬季，这与其他地区的研究结果较为类似[31,33]。三峡库区沉积物酸挥发性硫在季节和空间分布上表现出了较大差异(图 4)，这可能是因为酸挥发性硫对环境变化更敏感[34]。

5　结论

本文基于热蒸馏法，设计了一套连续提取沉积物还原性无机硫的装置和实验方法，该方法相比冷扩散法可较大地缩短单个还原性无机硫形态的提取时间；装置通过优化，设计了预先制备实验所需的二氯化铬溶液的步骤，实现了样品还原性无机硫形态的连续提取；并以过氧化氢为氧化剂，将提取的各形态硫氧化为 SO_4^{2-} 后采用离子色谱进行检测，操作简便、准确度高。同时，还应用本实验方法对长江三峡库区沉积物样品开展了还原性无机硫的分析研究，显示三峡库区硫污染程度相对较低。

本研究所设计的装置和方法解决了地质、环境调查研究中大批量样品需要快速、准确分析的问题，适合在相关行业推广应用。如何进一步通过装置和方法的优化，减少氮气吹脱量和提取反应的时间，则需要进一步开展实验研究。

Experimental Method and Application of Rapid and Continuous Extraction of Reduced Inorganic Sulfur from Sediments

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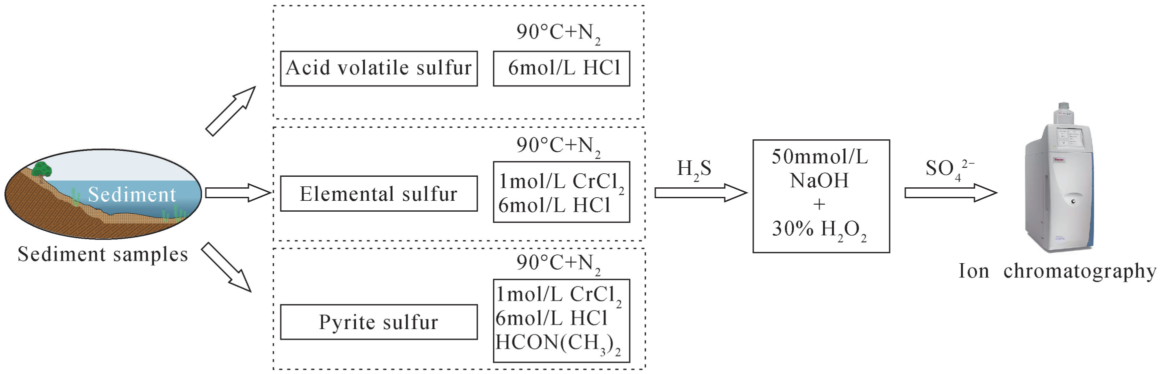
HIGHLIGHTS

(1) Continuous extraction of reduced inorganic sulfur from sediments was achieved.

(2) All forms of reduced inorganic sulfur were oxidized to SO_4^{2-} using H_2O_2 and then detected by ion chromatography.

(3) Three Gorges Reservoir sediments show low reduced inorganic sulfur content.



ABSTRACT

BACKGROUND: Sulfur is an active element with multiple chemical forms, which plays a vital role in the regulation of redox chemistry. Reduced inorganic sulfur (RIS) including acid volatile sulfur (AVS), elemental sulfur (ES) and pyrite sulfur (CRS) is the most active part of sulfur species in sediments and plays an important role in controlling the geochemical behavior of iron, phosphorus and heavy metals in sediments. Separation and determination of reduced inorganic sulfur in anoxic sediments are critical to ecological and geological studies of sulfur cycles.

Both distillation and diffusion methods can be effectively used to separate AVS, ES, and CRS in sediments. However, the current methods for extracting sulfur species are difficult to adapt to the large number of samples in geological and environmental research. Due to the reaction time, requirements of 24h for single sulfur species in the diffusion method limits the number of samples that can be processed on a timely basis. This limitation presents a problem for analyzing fresh anoxic sediment samples which have to be processed immediately to minimize the risk of sulfide re-oxidation. The detection method has the disadvantages of having a cumbersome testing process, long analysis time, and easy loss of sulfur components.

OBJECTIVES: To achieve efficient and continuous determination of reduced inorganic sulfur forms in bulk sediment samples.

METHODS: The method used in this experiment was improved based on the thermal distillation method, which was used to continuously extract the reduced inorganic sulfur from sediments. The reaction flask used in the experiment was a three-head round-bottom flask. A nitrogen flushing pipe, a condenser tube and two injection tubes were connected to each of the small necks. For the AVS procedure, 1.00g sediment sample reacted with 10mL of 6mol/L HCl under nitrogen gas at an elevated temperature (90℃) to convert reduced sulfur species into hydrogen sulfide which was subsequently carried by a nitrogen gas stream into a trap. For the CRS procedure, 20mL of $CrCl_2$ solution was added to the sediment in the distillation flask after the AVS procedure, and 10mL of 6mol/L HCl was immediately placed in the flask at an elevated temperature (90℃), flushed with nitrogen. For the ES procedure, 20mL DMF were poured into the sample flask which contained acid and $CrCl_2$ solutions from the previous procedure. 20mL of $CrCl_2$ solution and 10mL of 6mol/L HCl were injected into the flask, and the reaction was allowed to take place at 90℃ purging with nitrogen. During the entire distillation process, H_2S gas was absorbed by NaOH solution, and then oxidized by H_2O_2 to SO_4^{2-}. The concentrations of SO_4^{2-} were obtained by ion chromatography.

RESULTS: Repeatability experiments ($n = 3$) were conducted on sediment samples from the Three Gorges Reservoir area and the mean values of acid volatile sulfur, elemental sulfur and pyrite sulfur were obtained as 0.19, 0.37 and 3.10μmol/g, respectively. The relative standard deviations (RSD) of the experimental results were 5.26%, 1.22% and 3.09%, respectively. In order to test the effectiveness of the distillation procedures, $Na_2S \cdot 9H_2O$, pyrite and S were added in the sediment to reveal the corresponding standard recoveries. An average of 92.8% of the added $Na_2S \cdot 9H_2O$ was recovered by the AVS diffusion method. An average of 93.6% of the added pyrite was recovered by the CRS diffusion method. An average of 94.1% of the added elemental sulfur was recovered by the ES diffusion method. In the literature, recovery of AVS by the improved diffusion method ranged from 82.01% to 108.71%, and recovery of ES ranged from 92.25% to 98.08% ($n=3$), respectively.

The modified apparatus presented in this paper was an economic version which uses rubber and glass parts.

The method provided the advantages of lower sample weighing, and simple operation. Compared with the diffusion method (24h), the extraction time for individual sulfur forms by our distillation method was just 1.5h. The recoveries achieved by the method are comparable to those reported for earlier methods. In addition, the results are more like the data on reduced inorganic sulfur content obtained by Hongbin Yin after measuring sediment samples from Taihu Lake using the modified cold diffusion method, indicating that the method designed in this study has a high degree of confidence.

Geochemical processes of sulfur in river aquatic systems play a crucial role in environmental evolution. In this study, the distributions and seasonal variation of reduced inorganic sulfur (RIS) in the Three Gorges Reservoir area surface sediments were investigated. Surface sediment samples were collected from 8 points in the section from Yunyang to Zigui in the Three Gorges Reservoir area in August and December 2017. The result showed that the AVS and ES contents were higher in summer than in winter, and the trend of RIS in the section from Yunyang to Zigui was roughly decreasing, with obvious seasonal and spatial changes. Low sulfur pollution in the Three Gorges Reservoir area was observed.

CONCLUSIONS: The improved thermal distillation method and apparatus in this study have significant advantages in the extraction efficiency of reduced inorganic sulfur from sediments. The extraction time of this study for individual sulfur form is 1.5h, less than the diffusion method. The established analytical method has good precision and accuracy, which is suitable for investigation studies with large numbers of samples such as environmental research and geological surveys.

KEY WORDS: reduced inorganic sulfur; thermal distillation; sulfur species continuous extraction; sediment; ion chromatography

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