

王蕾, 于汀汀, 孙红宾, 等. 高压密闭酸溶-电感耦合等离子体发射光谱法测定硼矿石中的硼[J]. 岩矿测试, 2024, 43(3): 468–475. DOI: [10.15898/j.ykcs.202308070131](https://doi.org/10.15898/j.ykcs.202308070131).

WANG Lei, YU Tingting, SUN Hongbin, et al. Boron Analysis in Boron Ores by Inductively Coupled Plasma-Optical Emission Spectrometry with Sealed Acid Digestion at High Pressure[J]. Rock and Mineral Analysis, 2024, 43(3): 468–475. DOI: [10.15898/j.ykcs.202308070131](https://doi.org/10.15898/j.ykcs.202308070131).

高压密闭酸溶-电感耦合等离子体发射光谱法测定硼矿石中的硼

王蕾, 于汀汀, 孙红宾, 张保科*
(国家地质实验测试中心, 北京 100037)

摘要: 应用电感耦合等离子体发射光谱法 (ICP-OES) 分析硼矿石中的硼含量, 样品分解方法多采用酸溶法和熔融法, 硼酸在浓酸溶液中加热蒸发时形成易挥发的 BF_3 或 BCl_3 , 造成硼的损失。熔融法可分解难溶于酸的硅硼钙石、电气石等样品, 但将大量钠盐引入了样品中, 基体较大, 检出限高。本文建立了高压密闭酸溶-ICP-OES 测定硼矿石中硼含量的方法。样品经硝酸和氢氟酸在高压密闭溶样罐中分解完全、定容稀释后, 样品溶液用配备耐氢氟酸进样系统的 ICP-OES 测定。在 ICP-OES 中, 硼有三条常用分析谱线, 选取 249.677nm 为硼的分析谱线, 标准曲线的线性相关系数大于 0.9995。采用本方法对硼镁矿、锰方硼石和盐湖型固体硼矿三种类型 5 个不同含量范围的实际样品进行测定, 相对标准偏差 (RSD, $n=11$) 为 0.39%~2.66%, 方法检出限为 1.76 $\mu\text{g/g}$, 硼含量定量范围为 5.87 $\mu\text{g/g}$ ~10.8%。经标准物质验证, 硼含量测定值与标准值一致, 与容量法和微波消解法测定结果吻合。本方法试剂用量少, 无需蒸干样品溶液, 有效地避免了硼酸易挥发和试剂用量大的问题。

关键词: 硼矿石; 高压密闭酸溶; 电感耦合等离子体发射光谱法; 耐氢氟酸进样系统

要点:

- (1) 高压密闭酸溶消解硼矿石样品后无需赶酸, 提高了分析效率。
- (2) 应用氢氟酸进样系统进行测定, 解决了硼酸在浓酸溶液中加热蒸发时形成容易挥发的 BF_3 或 BCl_3 , 造成硼损失的问题。
- (3) 方法适用于硼镁矿、锰方硼石、盐湖型固体硼矿和硼镁铁矿类型样品, 可测定硼矿石中 11% 以下的硼含量。

中图分类号: O657.31

文献标识码: B

硼是一种典型的非金属元素, 也是非常分散的、典型的亲石元素, 分布于各种成因、不同类型的岩石中。硼在自然界分布广泛, 多成络阴离子 (BO_3^{3-} 、 $(\text{B}_2\text{O}_4)^{2-}$ 及 $(\text{BO}_4)^{5-}$ 形式存在于造岩矿物中, 亦可形成独立硼矿物。根据硼矿物的脉石矿物种类和主要矿物组分不同, 硼矿石类型划分为主要由蛇纹石、硅镁石、镁橄榄石等硅酸盐矿物组成的硅酸盐类硼矿石的脉石矿物, 以及主要由方解石、白云石、菱镁

矿、菱锰矿等碳酸盐矿物组成的碳酸盐类硼矿石的脉石矿物, B_2O_3 含量可高达 50%。硅酸盐类硼矿石是中国当前工业利用的主要矿石类型^[1]。准确测定硼矿石中硼的含量, 可为硼矿床的开发利用和选冶工艺研究、品位和储量评价以及集约节约开发利用相关矿产资源提供有力的技术支撑。

硼的测定方法较多, 除了经典的分光光度法^[2,3]、容量法^[4], 大批量地质化探样品一般采用

收稿日期: 2023-08-07; 修回日期: 2024-03-08; 接受日期: 2024-03-20

基金项目: 国家重点研发计划项目 (2021YFC2903000) 课题“战略性矿产多元素同时分析技术和标准化”

第一作者: 王蕾, 高级工程师, 从事地质样品分析方法研究与应用。E-mail: 13311060626@189.cn。

通信作者: 张保科, 高级工程师, 从事地质样品分析方法研究与应用。E-mail: zhangbaoke@mail.cgs.gov.cn。

光电直读发射光谱法^[5], 该方法不用分解样品, 分析速度快, 灵敏度高, 但由于是固体进样, 基体效应严重, 稳定性不高^[6]。电感耦合等离子体发射光谱法(ICP-OES)已在岩石、土壤、水系沉积物、植物、天然水等常规地质环境样品中的多元素分析中发挥了重要作用^[7-10], 也被广泛应用于测定样品中的硼含量^[6, 11-16]。硼矿石样品的分解多采用酸溶法和熔融法。硼酸在浓酸溶液中加热蒸发时形成容易挥发的BF₃或BCl₃, 造成硼损失。熔融法可分解难溶于酸的硅硼钙石、电气石等矿物, 但将大量钠盐引入样品中, 基体较大, 检出限高。李冰等^[17]用磷酸对样品中的硼加以保护, 解决了硼酸在浓酸溶液中容易挥发、造成损失^[18]的问题。方宏树等^[19]用过氧化钠作熔剂, 熔融地质样品中的硼后使用强酸性阳离子交换树脂, 交换溶液中大量的Na⁺, 降低了试液含盐量, 减小Ca²⁺、Mg²⁺、Al³⁺、Fe³⁺、K⁺等阳离子的干扰, 方法检出限为50μg/g。易田芳等^[20]建立了一种用硝酸、盐酸、氢氟酸和磷酸微波消解结合ICP-OES测定全硼含量的方法, 方法检出限为0.7mg/kg, 回收率为89.3%~96.5%。这些方法为硼元素的准确测定提供了借鉴, 但大多是对土壤和水系沉积物标准物质进行了测定, 硼含量范围为3.5~200μg/g。目前, 测定硼矿石中硼含量的方法还不多见。

本文以硼镁矿、锰方硼石、盐湖型固体硼矿和硼镁铁矿为研究对象, 使用氢氟酸和硝酸作为试剂, 采用高压密闭酸溶方法分解样品, 用耐氢氟酸进样系统的ICP-OES测定硼矿石中的硼含量, 有效地解决了熔融基体严重和酸溶硼易挥发损失的问题。

1 实验部分

1.1 仪器与工作条件

Optima 8300 电感耦合等离子体发射光谱仪(美国 PerkinElmer 公司), 配备耐氢氟酸的氧化铝中心管、雾化器和 Scott 雾室。仪器工作条件为: ICP 射频功率 1250W, 辅助气流速 0.2L/min, 冷却气流速 13.0L/min, 载气流速 0.5L/min, 氩气吹扫光路系统, 溶液提升量 1.5mL/min。

1.2 设备和主要试剂

分析天平: 感量 0.1mg。

密封溶样罐: 防腐溶样外套, 聚四氟乙烯内罐, 容积为 15mL。

电热恒温鼓风干燥箱: 最高工作温度 250℃, 控温精度±1℃。

硼标准溶液(硼浓度 1000μg/mL): 国家有色金属及电子材料分析测试中心研制。

硝酸、氢氟酸: 均为优级纯。实验用水符合 GB/T 6682 规定的二级水。

所使用器皿和设备应无硼干扰。

1.3 实验样品

自然界中, 硼矿分布很广, 已知含硼矿物约 150 余种。目前, 能加工利用的仅 20 余种^[21]。硼矿床类型有 5 种: ①沉积变质再造型镁橄榄岩、橄榄玄武岩和富镁大理岩中的硼矿床, 是中国硼矿床的主要类型; ②盐湖型硼矿床; ③接触交代型硼矿床; ④地下卤水型硼矿床; ⑤火山沉积型硼矿床。本文实验样品信息见表 1。按照《地质矿产实验室测试质量管理规范》(DZ/T 0130.2—2006) 的相关规定, 样品粒径应小于 0.097mm, 在 60℃ 预干燥 2h, 置于干燥器中, 冷却至室温。

表 1 实验用样品信息

Table 1 Information of experimental samples.

样品编号	采样地点	样品类型	硼含量 (%)
NBFB-1	辽宁宽甸	硼镁矿	10.8
NBFB-2	天津蓟县	锰方硼石	1.48
NBFB-3	辽宁宽甸	硼镁矿	7.77
NBFB-4	辽宁宽甸	硼镁矿	2.95
NBFB-5	青海大柴旦盐湖	盐湖型固体硼矿	0.27

1.4 实验方法

1.4.1 样品前处理

称取 0.1g 样品(精确到 0.1mg)置于聚四氟乙烯内罐中^[12, 22-23], 加入 2.0mL 硝酸和 2.0mL 氢氟酸, 盖上聚四氟乙烯上盖, 套上外套, 拧紧密封。将密封溶样罐放入干燥箱中, 于 190℃ 保温 24h。冷却后打开钢套, 取出聚四氟乙烯内罐, 将溶液移入 25.0mL 聚丙烯容量瓶中, 用水稀释至刻度摇匀, 此为试样溶液。分取 2.50mL 试样溶液置于 10.0mL 聚丙烯比色管中, 用水稀释至刻度摇匀, 此为上机测定溶液。随同制备样品空白溶液。

1.4.2 标准曲线的绘制

用硼标准溶液配制浓度分别为 0.00、5.00、10.0、20.0、50.0、100.0、150.0、200.0μg/mL 的硼校准标准溶液, 介质为硝酸-氢氟酸混合溶液。以校准溶液中硼元素的浓度值为横坐标, 谱线测定强度值为纵坐标, 绘制校准曲线。校准曲线一次拟合的相关系数 R²≥0.9995。

2 结果与讨论

2.1 分析谱线的选择

分析谱线的选择对实验数据准确测定产生直接影响。谱线选择要考虑元素检出限、共存元素干扰、背景干扰和线性范围等因素^[24]。在 ICP-OES 中,硼常用的谱线为 208.889nm、249.677nm 和 249.772nm,实验配制浓度为 0.00、10.0、20.0、50.0、100.0、200.0、300.0、500.0 μg/mL 的硼元素标准溶液,建立工作曲线,计算各条谱线的线性回归方程和线性相关系数,结果见表 2。谱线 208.889nm 强度最低,249.772nm 强度最高,考虑到样品含量较高,选取 249.677nm 作为硼的分析谱线。

表 2 硼标准溶液线性回归方程及线性相关系数

Table 2 Linear regression equation and linear correlation coefficient of boron standard solution.

硼元素分析谱线 (nm)	线性回归方程	线性相关系数 (R ²)
208.889	y=168.01x+43.037	1.0000
249.677	y=17635x+1474.1	1.0000
249.772	y=36192x+68547	0.9996

硼镁矿、硼镁铁矿、锰方硼石、盐湖固体硼矿中多含有硅、镁、锰、铁、钠等元素。实验配制了二氧化硅 100μg/mL,钠、锰、铁、镁各 1000μg/mL 的单元素标准溶液,研究上述元素对硼元素的干扰情况,实验结果表明未见明显干扰。

2.2 样品溶解试剂用量的确定

地质样品中的硼与硅稳定结合^[1],能否将硅铝结构打开,使样品溶解完全,关键在于氢氟酸的作用^[25-26]。实验以硼镁铁矿标准物质 (YSB 1674-05) 为研究对象,按照实验方法,称取 3 份样品,分别加入 0.5、1.0、2.0mL 氢氟酸溶解样品。测定结果表明,氢氟酸用量小于 1.0mL 时,硼的测定值偏低;氢氟酸用量大于 1.0mL 时,硼的测定值与标准值吻合。考虑到地质样品的复杂性,实验确定氢氟酸加入量为 2.0mL。

2.3 方法准确度

2.3.1 不同实验方法结果对比

采用本文方法和国家化工行业标准方法《硼镁矿石中三氧化二硼含量的测定 容量法》(HG/T 2956.3—2001) 及微波消解-电感耦合等离子体质谱法^[11,27]对硼镁铁矿标准物质 (YSB1674-05) 和硼硅酸盐玻璃标准物质 (GBW03132) 以及硼矿石实际样

品进行测定。测定结果 (表 3) 表明,在硼含量 10% 以内,本文方法与化工行业标准方法及微波消解方法测定结果一致。微波消解仪较高压密闭罐的成本高、不易清洗^[28-29],实验工作者可根据实验室情况进行合理选择。

表 3 本文方法与容量法、微波消解法测定硼含量结果对比

Table 3 Comparison of boron content determined by this method, volumetric method and microwave digestion method.

标准物质和 实际样品 编号	硼含量标准值 (%)	硼含量测定值 (%)		
		本文方法	容量法	微波消解法
YSB1674-05	1.75±0.047	1.74	1.73	1.74
GBW03132	2.75±0.034	2.74	2.77	2.76
NBFB-1	—	10.9	10.9	10.8
NBFB-3	—	7.75	7.82	7.80

2.3.2 样品百分总和计算结果

用百分总和检查硅酸盐岩石全分析数据的质量是分析工作者的传统做法^[30-31]。采用本文方法测定硼元素含量,用《硅酸盐岩石化学分析方法 第 28 部分: 16 个主次成分量测定》(GB/T 14506.28—2010) X 射线荧光光谱法测定除硼以外的主量元素,用《硅酸盐岩石化学分析方法 第 34 部分: 烧失量的测定 重量法》(GB/T 14506.34—2019) 测定烧失量 (LOI), 对各测定值进行百分总和计算,结果见表 4。因样品 NBFB-2 是锰方硼石 (Mn₃B₇O₁₃Cl), 样品 NBFB-5 中含 SO₃ 不适用于此方法进行百分总和检查,其他样品中的主量元素各项结果的加和 (99.5% ~ 100.2%) 能够达到《地质矿产实验室测试质量管理规范》的一级标准 (99.3% ~ 100.7%) 要求。

2.4 方法检出限和测定下限

在最优工作条件下,按照实验方法,连续测定 11 次流程空白溶液,结果分别为: 1.86、1.25、0.27、1.42、0.31、0.39、0.18、0.35、1.07、1.03、1.43μg/g。以测定结果的 3 倍标准偏差计算方法检出限为 1.76μg/g,以 10 倍标准偏差计算方法测定下限为 5.87μg/g,与传统 ICP-OES 酸溶法的检出限相当,优于熔融法。

2.5 方法精密度

按照实验方法,选取硼含量在 0.27% ~ 10.8% 的 5 个不同含量范围的实际样品进行平行测定,11 次测定的相对标准偏差 (RSD, n=11) 为 0.39% ~ 2.66% (表 5)。

表 4 样品百分总和结果

Table 4 Aggregation results of samples.

实际样品 编号	主量元素和烧失量测定值 (%)												加和 (%)
	Al ₂ O ₃	CaO	TFe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	B ₂ O ₃	LOI	
NBFB-1	0.68	3.50	6.32	0.36	37.5	0.39	0.03	0.06	2.81	0.05	34.8	13.0	99.5
NBFB-2	3.73	7.82	2.03	2.30	4.47	21.8	0.07	0.10	26.0	0.14	4.77	22.9	96.2
NBFB-3	1.51	3.40	5.06	0.90	37.2	0.29	0.08	0.63	16.4	0.05	24.8	9.81	100.2
NBFB-4	0.06	1.91	0.40	0.01	46.3	0.08	0.04	0.04	5.29	0.01	9.60	36.1	99.9
NBFB-5	2.88	15.2	1.03	0.81	18.4	0.05	3.49	0.04	16.5	0.13	0.87	37.9	97.2

表 5 方法精密度

Table 5 Precision test of the method.

实际样品 编号	硼含量测定值 (%)						RSD (%)
	11 次分次测定值					平均值	
NBFB-1	10.80	10.72	10.80	10.84	10.79	10.80	0.39
	10.80	10.76	10.80	10.86			
	10.86	10.77					
NBFB-2	1.48	1.49	1.50	1.49	1.47	1.48	0.81
	1.50	1.49	1.47	1.46	1.47		
NBFB-3	7.71	7.73	7.73	7.82	7.73	7.77	0.82
	7.87	7.86	7.71	7.86	7.75		
NBFB-4	3.00	3.08	2.91	3.04	2.96	2.95	2.66
	3.03	2.82	2.92	2.89	2.89		
NBFB-5	0.26	0.27	0.26	0.27	0.26	0.27	2.23
	0.28	0.27	0.26	0.27	0.27		

3 结论

通过方法实验研究、标准物质验证、不同方法比对等,建立了高压密闭酸溶-电感耦合等离子体发射光谱测定硼矿石中硼含量的方法。该方法用硝酸和氢氟酸分解样品,用配备耐氢氟酸进样系统的 ICP-OES 进行测定,解决了酸溶硼易挥发损失、熔融样品基体过大的问题,与传统方法相比,试剂用量少,基体干扰小,分析效率高,可满足硼矿石中硼含量分析需求。

本方法在使用中,只涉及常规的试剂、器皿、密闭溶样罐及电感耦合等离子体发射光谱仪,适宜推广普及。但由于硼矿石标准物质较少,本方法是否能溶解更多类型的硼矿石以及方法的测定上限,还有待进一步研究。

Boron Analysis in Boron Ores by Inductively Coupled Plasma-Optical Emission Spectrometry with Sealed Acid Digestion at High Pressure

WANG Lei, YU Tingting, SUN Hongbin, ZHANG Baoke*
(National Research Center for Geoanalysis, Beijing 100037, China)

HIGHLIGHTS

- (1) There is no need to expel acid after sealed acid digestion of boron ore at high pressure, which effectively improves the analytical efficiency.
- (2) The problem of BF₃ or BCl₃, which is easily volatilized when boric acid is heated and evaporated in concentrated acid solution, is solved by using a hydrofluoric acid-resistant sampling system.
- (3) The method is suitable for the samples of boromagnesite, chambersite, salt lake type solid boron ore and ludwigite, and the content of boron in boron ores below 10% can be determined.

ABSTRACT: The literature provides reference for the accurate determination of boron by inductively coupled plasma-optical emission spectrometry (ICP-OES), but most of the studies are conducted on the standard substances of soil and stream sediment. In addition, the range of boron content is low, and the methods for the determination of high boron content in boron ores are few. A method of ICP-OES with sealed acid digestion at high pressure was developed for the determination of boron content in boron ores. Using nitric acid and hydrofluoric acid as reagents, the samples of boron ores were dissolved at high temperature and high pressure without acid drive, and ICP-OES equipped with a hydrofluoric acid-resistant sampling system was used to determine boron. The samples of boromagnesite, ludwigite, chambersite and salt lake type solid boron ore were taken as the research objects. The relative standard deviation (RSD, $n=11$) was 0.39%–2.66%, the detection limit of the method was 1.76 $\mu\text{g/g}$, and the determination range was 5.87 $\mu\text{g/g}$ –10.8%. The measured values were consistent with the certified values after the verification of the reference materials. Compared with volumetric method and microwave digestion method, the results were in good agreement. This method does not require evaporating the sample solution, which solves the boron volatile loss problem. The BRIEF REPORT is available for this paper at <http://www.ykcs.ac.cn/en/article/doi/10.15898/j.ykcs.202308070131>.

KEY WORDS: boron ore; sealed acid digestion at high pressure; inductively coupled plasma-optical emission spectrometry; hydrofluoric acid-resistant sampling system

BRIEF REPORT

Significance: The exploitation and utilization of boron resources play an important role in the development of modern industry. The accurate determination of boron content in boron ores provides powerful technical support for the utilization and the smelting technology study of boron ore deposit. Inductively coupled plasma-optical emission spectrometry (ICP-OES) has been widely used in the determination of boron content in samples due to its advantages of high accuracy and sensitivity, wide linear range, low detection limit and good precision. At present, most of the studies focus on the boron determination of the standard substances in soil and stream sediment with a narrow determination range; the methods for the determination of high boron content in boron ores are few. In the research, a method of ICP-OES was developed for the determination of boron content in boron ores with sealed acid solution digestion at high pressure and a hydrofluoric acid-resistant sampling system. The method satisfies the determination requirements, with advantages of using less reagent and avoiding boron loss.

Methods: A high pressure sealed acid digestion-ICP-OES method was developed for the determination of boron in boron ores, through systematic experimental research, reference material verification, and comparison of different methods. Using nitric acid and hydrofluoric acid as reagents, the sample of boron ore was dissolved at high temperature and high pressure without acid drive, and ICP-OES equipped with a hydrofluoric acid-resistant sampling system was used to determine boron. This method solved the problem of forming volatile BF_3 or BCl_3 when boric acid was heated and evaporated in concentrated acid solution, which caused loss.

Data and Results: The samples of boromagnesite, ludwigite, chambersite and salt lake solid boron ore were taken as the research objects, the measuring spectrum lines and the amount of reagents were studied. The results show that in boron ores, there was no interference of Si, Mg, Mn, Fe, Na or other elements on the three commonly used analytical spectral lines of boron in ICP-OES. The linear correlation coefficient (R^2) of spectral lines was greater than 0.9995. The analytical spectral line of 249.677nm with moderate intensity was selected for boron. When the amount of hydrofluoric acid was greater than 1.0mL, the measured value was consistent with the certified value of the reference material. Considering the complexity of the geological sample, the experiment determined that the addition amount of hydrofluoric acid was 2.0mL. According to the experimental method, 5 actual samples with varying content of three types of boromagnesite, chambersite and salt lake solid boron ore were selected for

determination. The relative standard deviation (RSD, $n=11$) was 0.39%–2.66%, the detection limit of the method was 1.76 $\mu\text{g/g}$, and the determination range was 5.87 $\mu\text{g/g}$ –10.8%. The measured values were consistent with the certified values after the verification of the reference materials. Compared with volumetric method and microwave digestion method, the results were in good agreement. The repeatability and reproducibility of the method were verified by the precision collaborative experiments among the ten laboratories. The method only involves conventional reagents, vessels, high-pressure digestion tanks and ICP-OES instrument, which is suitable for popularization.

参考文献

- [1] 《岩石矿物分析》编委会. 岩石矿物分析 (第四版 第二分册)[M]. 北京: 地质出版社, 2011: 376–396.
The editorial committee of “Rock and Mineral Analysis”. Rock and Mineral Analysis (The 4th edition, Volume II) [M]. Beijing: Geological Publishing House, 2011: 376–396.
- [2] 于微. 分光光度法测定水系沉积物中硼[J]. 吉林地质, 2014, 33(4): 61–63.
Yu W. Determination of boron in stream sediments by spectrophotometric method[J]. Jilin Geology, 2014, 33(4): 61–63.
- [3] 邢书才, 杨永, 岳亚萍. 姜黄素分光光度法测定水中硼的优化检测条件研究[J]. 中国测试, 2019, 45(6): 65–69.
Xing S C, Yang Y, Yue Y P. Study on the optimizing conditions for determining boron in water by curcumin spectrophotometry[J]. China Measurement & Test, 2019, 45(6): 65–69.
- [4] 赵志刚, 韦雪梅, 赵华丽. 高氯酸消解电位滴定法测定硼粉纯度[J]. 化学分析计量, 2022, 31(6): 46–49.
Zhao Z G, Wei X M, Zhao H L. Determination of the purity of boron powder by potentiometric titration after sample digested by perchloric[J]. Chemical Analysis and Meterage, 2022, 31(6): 46–49.
- [5] 王顺祥, 龚仓, 吴少青, 等. 固体进样-CCD 光电直读发射光谱法测定地球化学样品中微量银、硼和锡[J]. 中国无机分析化学, 2023, 13(8): 863–868.
Wang S X, Gong C, Wu S Q, et al. Determination of trace silver, boron and tin in geochemical samples by CCD optical direct-reading emission spectrometer with solid injection[J]. Chinese Journal of Inorganic Analytical Chemistry, 2023, 13(8): 863–868.
- [6] 张元, 王文东, 卢兵, 等. 碱熔-阳离子交换树脂分离 ICP-MS 法测定厚覆盖区地球化学调查样品中硼锆镨钼锡碘钨[J]. 岩矿测试, 2022, 41(1): 99–108.
Zhang Y, Wang W D, Lu B, et al. Determination of boron, germanium, bromine, molybdenum, tin, iodine and tungsten in geochemical survey sample by ICP-MS with alkali fusion-cation exchange resin separation[J]. Rock and Mineral Analysis, 2022, 41(1): 99–108.
- [7] Manousi N, Kabir A, Furton K G, et al. Dual lab-in-syringe flow-batch platform for automatic fabric disk sorptive extraction/back-extraction as a front end to inductively coupled plasma atomic emission spectrometry[J]. Analytical Chemistry, 2022, 94(38): 12943–12947.
- [8] Vievard J, Amoikon T L, Coulibaly N A, et al. Extraction and quantification of pesticides and metals in palm wines by HS-SPME/GC-MS and ICP-AES/MS[J]. Food Chemistry, 2022, 393: 133352.
- [9] Zeng Y, Yokoyama Y, Hirabayashi S, et al. A rapid and precise method of establishing age model for coral skeletal radiocarbon to study surface oceanography using coupled X-ray photos and ICP-AES measurement[J]. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2022, 533: 23–28.
- [10] Erickson B. Product review: ICP-AES remains competitive[J]. Analytical Chemistry, 1998, 70(5): 211A–215A.
- [11] 刘向磊, 孙文军, 任彧仲, 等. 微波消解 混合模式电感耦合等离子体质谱法测定土壤或沉积物中银、锡、硼[J]. 质谱学报, 2022, 43(4): 522–532.
Liu X L, Sun W J, Ren Y Z, et al. Determination of silver, tin and boron in soil or sediment sample with microwave digestion by mixed mode inductive coupled plasma mass spectrometry[J]. Journal of Chinese Mass Spectrometry Society, 2022, 43(4): 522–532.
- [12] 刘跃, 王记鲁, 李静, 等. 高压密闭消解-电感耦合等离

- 子体质谱(ICP-MS)法测定土壤背景点样品中的29种元素[J]. 中国无机分析化学, 2023, 13(2): 136-142.
- Liu Y, Wang J L, Li J, et al. Determination of 29 elements in soil background site samples by inductively coupled plasma mass spectrometry with high pressure closed digestion[J]. Chinese Journal of Inorganic Analytical Chemistry, 2023, 13(2): 136-142.
- [13] 赵庆令, 李清彩, 蒲军, 等. 电感耦合等离子体发射光谱法同时测定土壤样品中砷硼铈碘铌硫钪锆钽钨等31种元素[J]. 岩矿测试, 2010, 29(4): 455-457.
- Zhao Q L, Li Q C, Pu J, et al. Simultaneous determination of 31 elements in soil samples by inductively coupled plasma-atomic emission spectrometry[J]. Rock and Mineral Analysis, 2010, 29(4): 455-457.
- [14] 杜宝华, 盛迪波, 王日中, 等. 电感耦合等离子体发射光谱(ICP-OES)法测定含硼聚乙烯核屏蔽材料中的硼[J]. 中国无机分析化学, 2023, 13(3): 274-277.
- Du B H, Sheng D B, Wang R Z, et al. Determination of boron content in boron-containing polyethylene nuclear shielding materials by ICP-OES[J]. Chinese Journal of Inorganic Analytical Chemistry, 2023, 13(3): 274-277.
- [15] 方宏树, 孔晓彦, 胡兰基. ICP-OES法测定盐湖土壤中锂和硼的方法研究[J]. 当代化工, 2023, 52(1): 248-252.
- Fang H S, Kong X Y, Hu L J. Study on the determination method of lithium and boron in salt lake soil by ICP-OES[J]. Contemporary Chemical Industry, 2023, 52(1): 248-252.
- [16] 黄合生, 邢文青, 黄波, 等. ICP-AES法测定凝渣剂中铝和硼元素含量[J]. 南方金属, 2023, 250: 19-23.
- Huang H S, Xing W B, Huang B, et al. Determination of aluminum and boron in slag coagulant by inductively coupled plasma[J]. South Metals, 2023, 250: 19-23.
- [17] 李冰, 马新荣, 杨红霞, 等. 封闭酸溶-电感耦合等离子体原子发射光谱法同时测定地质样品中砷硼硫[J]. 岩矿测试, 2003, 22(4): 241-247.
- Li B, Ma X R, Yang H X, et al. Determination of boron, arsenic and sulfur in geological samples by inductively coupled plasma atomic emission spectrometry with sample treatment by pressurized decomposition[J]. Rock and Mineral Analysis, 2003, 22(4): 241-247.
- [18] Zarcinas B A, Cartwright B. Acid dissolution of soils and rocks for the determination of boron inductively coupled plasma atomic emission spectrometry[J]. Analyst, 1987, 112(8): 1107-1112.
- [19] 方宏树, 何媛媛, 鲁海妍. 过氧化钠熔融 ICP-OES 法测定地矿样品中的硼[J]. 化学工程师, 2023(1): 24-28.
- Fang H S, He Y Y, Lu H Y. Determination of boron in geological and mineral samples by sodium peroxide melting ICP-OES[J]. Chemical Engineer, 2023(1): 24-28.
- [20] 易田芳, 向勇, 蒋建军, 等. 四酸微波消解-电感耦合等离子体发射光谱(ICP-OES)法测定土壤和沉积物中全硼含量[J]. 中国无机分析化学, 2023, 13(6): 576-581.
- Yi T F, Xiang Y, Jiang J J, et al. Determination of total boron in soil and deposit by inductively coupled plasma optical emission spectroscopy with four acids-microwave digestion[J]. Chinese Journal of Inorganic Analytical Chemistry, 2023, 13(6): 576-581.
- [21] 《矿产资源工业要求手册》编委会. 矿产资源工业要求手册[M]. 北京: 地质出版社, 2012.
- [22] 肖凡, 张宁, 姜云军, 等. 密闭酸溶-电感耦合等离子体原子发射光谱法测定地球化学调查样品中硼[J]. 冶金分析, 2018, 38(6): 50-54.
- Xiao F, Zhang N, Jiang Y J, et al. Determination of boron in geochemical survey sample by inductively coupled plasma atomic emission spectrometry after acid dissolution in closed system[J]. Metallurgical Analysis, 2018, 38(6): 50-54.
- [23] 王蕾, 张保科, 马生凤, 等. 封闭压力酸溶-电感耦合等离子体光谱法测定钨矿石中的钨[J]. 岩矿测试, 2014, 33(5): 661-664.
- Wang L, Zhang B K, Ma S F, et al. Determination of wolfram in tungsten ore by pressurized acid digestion-inductively coupled plasma-atomic emission spectrometry[J]. Rock and Mineral Analysis, 2014, 33(5): 661-664.
- [24] 叶家瑜, 江宝林. 区域地球化学勘查样品分析方法[M]. 北京: 地质出版社, 2004: 226-227.
- [25] 金佳旭, 郑旭, 付彦吉, 等. 不同酸液作用下牛蹄塘组页岩孔隙结构演化特征试验研究[J]. 工程地质学报, 2021, 29(3): 891-900.
- Jin J X, Zhen X, Fu Y J, et al. Experimental study of acidization impact to pore topological structure variation of Niutitang shale[J]. Journal of Engineering Geology,

- 2021, 29(3): 891–900.
- [26] 印万忠. 氢氟酸在硅酸盐矿物浮选中的作用机制[J]. 黄金学报, 1999, 1(4): 271–274.
- Yin W Z. Effect mechanism of hydrofluoric acid in flotation of silicate minerals[J]. Gold Journal, 1999, 1(4): 271–274.
- [27] 杨林, 邹国庆, 周武权, 等. 微波消解-电感耦合等离子体质谱 (ICP-MS) 法测定稀有多金属矿中锂铍铌钽铷铯[J]. 中国无机分析化学, 2023, 13(8): 825–830.
- Yang L, Zou G Q, Zhou W Q, et al. Determination of Li, Be, Nb, Ta, Rb, Cs in rare polymetallic ores by inductively coupled plasma mass spectrometry (ICP-MS) with microwave digestion[J]. Chinese Journal of Inorganic Analytical Chemistry, 2023, 13(8): 825–830.
- [28] 朱健, 马程程, 赵磊, 等. 高压密闭消解-电感耦合等离子体质谱法测定煤中 17 种金属元素[J]. 理化检验 (化学分册), 2014, 50(8): 960–963.
- Zhu J, Ma C C, Zhao L, et al. ICP-MS determination of 17 metal elements in coal with high-pressure closed digestion[J]. Physical Testing and Chemical Analysis (Part B: Chemical Analysis), 2014, 50(8): 960–963.
- [29] 马亮帮, 张大勇, 腾格尔, 等. 高压密闭消解-电感耦合等离子体质谱 (ICP-MS) 法测定煤中稀土元素[J]. 中国无机分析化学, 2019, 9(4): 27–30.
- Ma L B, Zhang D Y, Tenger, et al. Determination of rare earth elements in coal by inductively coupled plasma-mass spectrometry with high-pressure closed digestion[J]. Chinese Journal of Inorganic Analytical Chemistry, 2019, 9(4): 27–30.
- [30] 李迎春, 周伟, 王健, 等. X 射线荧光光谱法测定高铈高钡的硅酸盐样品中主量元素[J]. 岩矿测试, 2013, 32(2): 249–253.
- Li Y C, Zhou W, Wang J, et al. Determination of major elements in silicate samples with high content strontium and barium by X-ray fluorescence spectrometry[J]. Rock and Mineral Analysis, 2013, 32(2): 249–253.
- [31] 李迎春, 张磊, 周伟, 等. 熔融制样-波长色散和能量色散 X 射线荧光光谱仪应用于硅酸盐类矿物及疑难样品分析[J]. 岩矿测试, 2020, 39(6): 828–838.
- Li Y C, Zhang L, Zhou W, et al. Determination of major and minor elements in rock, soils and sediments and complex samples by wavelength and energy dispersive X-ray fluorescence Spectrometry with fusion sampling[J]. Rock and Mineral Analysis, 2020, 39(6): 828–838.