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镍锍试金富集-电感耦合等离子体质谱法测定地质样品中超痕量铂族元素

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摘要：铂族元素 (PGEs) 六项元素钌、铑、钯、锇、铱和铂的物理化学性质相近，在地壳中丰度极低且分布不均匀，且具有明显的粒金效应，长期以来准确测定其含量始终是岩矿测试的难题。镍锍试金取样量大，可定量分离富集铂族元素，通常被应用于 PGEs 分析，但将其应用于超痕量 PGEs 分析的关键问题是流程空白高，质谱干扰严重。本文报道了一种同时测定样品中超痕量铂钯铑铱锇和钌的方法。检查全流程试剂空白后，使用镍锍试金富集样品中的 PGEs，经杂质分离，利用电感耦合等离子体质谱 (ICP-MS) 动能歧视模式测定六项元素，有效地降低了质谱干扰。结果表明，方法的空白主要来自盐酸和捕集剂镍粉，选择合适厂家的试剂或对试金配料进行提纯，可降低全流程空白。同时，使用 ICP-MS 法测定六项元素时，在标准模式下，铂和钯的检出限小于 0.2ng/g，铑、铱和锇的检出限小于 0.02ng/g，钌的检出限大于 0.1ng/g，钌的检出限无法满足超痕量 PGEs 的测定要求。使用动能歧视模式后，钌的背景等效浓度比标准模式降低近两个数量级，从而消除了镍对钌的质谱干扰，钌的检出限降低至 0.005ng/g，使六项元素检出限同时满足超痕量 PGEs 测定要求。该方法用于分析土壤 (GBW07288、GBW07294)、水系沉积物标准物质 (GBW07289)，六项元素的结果与标准值符合，相对误差为−10.9%～11.8%，相对标准偏差为 3.85%～9.37%，加标回收率为 92%～110%。该方法流程较短、操作简便，满足大批量地质样品中超痕量 PGEs 的检测要求。

关键词：镍锍试金；电感耦合等离子体质谱法；动能歧视模式；铂族元素；土壤；水系沉积物

要点：

(1) 通过对锍镍试金配料及各类溶剂空白值的检验，确定空白来源及试剂提纯方法，并采用羰基镍粉有效地降低全流程空白，使痕量铂族六项元素的检出限满足地球化学调查需求。

(2) 通过添加羰基铁粉，优化试金配方，使锍扣在水浸泡的条件下即可自行粉化松散，不仅简化了分析流程，而且避免了因机械碎扣而产生污染的风险。

(3) 采用动能歧视模式测定，有效地消除镍元素的质谱干扰，降低钌元素的背景等效浓度约两个数量级，提高了检测结果的准确性。

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铂族元素 (PGEs) 具有优良的理化性能，被广泛应用于航空航天、特种功能材料、催化剂、电化学等尖端技术领域，是重要的战略性矿产资源。近年来，随着中国高新技术和航空航天的飞速发展，对铂族金属的需求空前高涨，铂族元素的准确测定能够为地质找矿提供重要技术支撑[1-2]。

铂族元素通常分布在非均质的微矿物相中，多以金属或金属互化物的形式存在，由于其在矿物中分布极不均匀且有明显的粒金效应，因此需要增大样品取样量来保证代表性。在样品的分解过程中，锇和钌易形成挥发性四氧化锇和四氧化钌，通常采用强碱保护熔融-蒸馏的方法进行测定，但该方法无法同时测定铂族六项元素[3-5]。漆亮等[6]、赵正等[7]使用改进的卡洛斯管结合高压釜的溶样方法，解决了锇和钌的挥发问题。该方法中试剂用量少，空白低，而且在电感耦合等离子体质谱 (ICP-MS) 测定前，使用阳离子交换树脂去除铜和镍等阳离子，有效地解决了质谱干扰问题，能够同时测定铂族六项元素，但流程较为复杂，不适合大批量地质样品分析测试。镍锍试金可有效地富集数十克地质样品中的铂族元素，与具有高灵敏度的 ICP-MS 相结合，能够很好地降低方法检出限[8-15]；但应用在超痕量铂族元素分析中仍面临很大困难，最关键的问题是镍锍试金全流程空白较高。为实现 0.1ng/g 样品的准确测定，需要降低试剂空白并优化测定模式。吕彩芬等[16]、毛香菊等[17]、Ni 等[18]在镍锍试金全流程空白方面开展了大量工作，对镍锍试金的空白来源进行了讨论，并对各种提纯镍方法的效果和实用性进行了对比。其中，试金-碲共沉淀法对镍的提纯效果最好，实际操作简单易行，将试金滤液合并后经碳酸镍沉淀、洗涤、干燥、焙烧后可得纯氧化镍，而且氧化镍可以循环使用，既降低了成本又解决了废液的排放问题。该方法的缺点是采用ICP-MS 标准模式测定铂族元素，待测溶液中残留的铜和镍会严重干扰钌和钯的测定。

本文对镍锍试金配料及各类溶剂空白值进行检验，确定空白来源及试剂提纯方法，降低全流程空白。利用镍锍试金富集铂族元素，试金过程中，加入羰基铁粉，使锍扣在水浸泡的条件下自行粉化松散，以简化分析流程，且避免因机械碎扣而产生污染的风险。采用 ICP-MS 动能歧视模式测定待测溶液，通过消除多原子离子干扰降低方法检出限[19-21]。

1 实验部分

1.1 标准溶液和主要试剂

钌、铑、钯、锇、铱、铂单元素标准储备溶液：100μg/mL(购自北京钢铁研究总院)。分取钌、铑、钯、锇、铱、铂单元素标准储备溶液，逐级稀释，配制成钌、铑、锇、铱浓度为 0.1、0.5、1.0、5.0、10.0ng/mL，铂和钯浓度为 1.0、5.0、10.0、50.0、100.0ng/mL 混合标准工作溶液，王水 (10%) 介质，保存期为两周。

镥标准溶液：100μg/mL(购自中国计量科学研究院)。分取镥标准溶液稀释配制内标溶液，Lu 浓度为 10ng/mL，3% 硝酸介质。

碳酸钠 (工业纯)，粉状；硼砂 (工业纯)，粉状；二氧化硅 (分析纯)，粉状；羰基镍 (工业纯)，粉状；羰基铁 (工业纯)，粉状；面粉 (食用级)；升华硫 (分析纯)；覆盖剂 (3∶1)：轻质氧化镁 (分析纯)+碳化硅 (分析纯)；盐酸 (分析纯)；硝酸 (分析纯)；王水。

实验用水为去离子水。

1.2 主要仪器和装置

Agilent 7900 型电感耦合等离子体质谱仪 (美国 Agilent 公司)，测定前使用 Li、Co、Y、Tl 混合调谐液对仪器调谐至双电荷产率小于 3%，氧化物产率小于 2%，使仪器的强度、灵敏度均达到最优。ICP-MS 仪器工作参数见表 1。

表 1　ICP-MS 仪器工作参数

Table 1　Working parameters of ICP-MS instrument.

工作参数	设定值	工作参数	设定值
射频功率	1550W	冷却气流速	15L/min
采样深度	8mm	载气流速	1L/min
雾化室温度	2℃	辅助气流速	1L/min
提取透镜电压	−165V	碰撞气 (He) 流速	3.6L/min

GWL-1400℃ 试金炉 (洛阳炬星窑炉有限公司)；试金坩埚 (黏土)。

1.3 实验方法

1.3.1 试金配料的配制

地质样品主要包括土壤和水系沉积物，根据不同样品的物质组成特征按表 2 配制试金配料。

1.3.2 样品的熔融

称取样品 20g 与试金配料充分混匀后放入试金坩埚，并均匀覆盖 20g 覆盖剂。坩埚置于升温至 1050℃ 的高温炉中，待炉温回升到 1050℃ 后计时 30min，取出坩埚，将熔融体倒入铁模中，冷却后敲碎

玻璃渣滓, 取出锍扣。

1.3.3　锍扣的分解

将锍扣放入磨口锥形瓶中, 用 20mL 水浸泡锍扣, 至粉化松散后加入 20mL 盐酸, 加装风冷管, 150℃低温微沸分解至溶液清亮且不再冒气泡。

1.3.4　样品中铂族元素的测定

采用滤膜过滤, 用 50℃ 左右的 10% 热盐酸反复冲洗沉淀。将沉淀及滤膜转入原磨口锥形瓶, 加入 5mL 王水, 加装风冷管, 于 150℃ 加热至完全溶解, 冷却后定容至 25mL 容量瓶中, 摇匀, 以三通在线加入铯 (10ng/mL) 为内标, ICP-MS 动能歧视模式测定。

2　结果与讨论

2.1　试剂空白及提纯

2.1.1　盐酸中的铂族空白及提纯方法

根据实验方法, 取 50mL 不同厂家 (记为Ⅰ和Ⅱ)、不同纯度盐酸, 低温蒸干, 加入使用相同批次盐酸制备的王水 5mL, 低温提取, 再加入 20mL 水, ICP-MS 测定, 按 20g 取样量计算。从表 3 中数据可见, 盐酸中含有一定量的铂、钯和钌, 样品分析前要检查盐酸空白, 当盐酸空白超过 0.02ng/g 时, 无法进行超痕量铂族元素分析。

盐酸提纯: 取 1000mL 盐酸, 加热后, 加入 1g/L 亚碲酸钾溶液 5mL, 滴加 1mol/L 氯化亚锡 (6mol/L 盐酸介质) 至产生大量黑色沉淀, 加热煮沸, 使沉淀凝聚, 过滤后再重复沉淀一次, 即可得到空白较低的盐酸。

2.1.2　熔剂二氧化硅中的铂族空白

取不同厂家 (记为Ⅲ和Ⅳ)、不同纯度的二氧化硅 10g, 加入 40mL 王水 (50%), 煮沸 2h, 过滤, 滤液低温蒸干, 加入 5mL 王水溶解沉淀, 加入 20mL 水, ICP-MS 测定。结果表明两个厂家的分析纯二氧化硅和优级纯二氧化硅所引入的铂族六项元素全流程空白均低于 0.01ng/g, 能满足铂族六项元素含量在 0.1ng/g 级别地质样品的测定需求, 对镍锍试金全流程空白的影响可忽略不计。

2.1.3　其他熔剂中的铂族空白

按照实验方法, 固定羰基镍粉用量不变, 按比例混匀碳酸钠、硼砂、硫粉、羰基铁粉和面粉, 分别取 20、40、60、80g 混合熔剂, 按照试金流程处理和测定。从表 4 中数据可见, 当碳酸钠、硼砂、硫粉、羰基铁和面粉用量呈整数倍增加时, 对应的铂族六项元素流程空白测定结果没有增大, 说明试剂空白对镍锍试金全流程空白贡献很小。

2.1.4　捕集剂中的铂族空白及提纯方法

固定其他熔剂, 分别加入不同厂家生产的氧化镍、硝酸镍和羰基镍 (Ⅴ和Ⅵ), 按照实验方法熔融、捕集、测定铂族元素。从表 5 中数据可见, 不同镍粉中铂族元素的含量差别较大。根据上述实验结果, 可以认为全流程空白主要来自镍粉。

镍提纯: 取 10g 氧化镍溶解于 30mL 盐酸中, 加入 0.5g/L 亚碲酸钾溶液 4mL, 滴加 1mol/L 氯化亚锡溶液至产生黑色沉淀, 再多加 2mL, 加热 1h 使沉淀凝聚, 冷却后用 0.45μm 滤膜过滤。滤掉杂质后, 将滤液在电热板上加热浓缩至较小体积, 加入碳酸钠中和至 pH=8, 产生碳酸镍沉淀, 水洗至中性, 离心, 弃清液, 将沉淀转入瓷皿, 于 105℃ 烘干, 再放入马弗炉, 于 500℃ 焙烧 2h, 即可得空白较低的氧化镍粉末。

表 2　镍锍试金配料组成

Table 2　Composition of nickel sulfide fire assay ingredients.

样品类型	称样量 (g)	硫 (g)	羰基镍 (g)	羰基铁 (g)	硼砂 (g)	碳酸钠 (g)	二氧化硅 (g)	面粉 (g)
土壤	20	2	1.6	4	25	20	5	1
水系沉积物	20	2	1.6	4	25	20	6	1

表 3　不同盐酸对应的流程空白

Table 3　Blank values corresponding to different classes of hydrochloric acid.

试剂	Ru (ng/g)	Rh (ng/g)	Pd (ng/g)	Os (ng/g)	Ir (ng/g)	Pt (ng/g)
Ⅰ-分析纯	0.0350	0.0003	0.0023	0.0006	<0.0001	0.0019
Ⅰ-优级纯	0.0346	0.0004	0.0013	0.0005	<0.0001	0.0015
Ⅱ-分析纯	0.0018	0.0001	0.0016	0.0002	<0.0001	0.0012
Ⅱ-优级纯	0.0015	0.0002	0.0013	0.0002	<0.0001	0.0011

表 4　不同熔剂用量对应的流程空白

Table 4　Blank values corresponding to different amounts of flux.

熔剂用量 (g)	Ru (ng/g)	Rh (ng/g)	Pd (ng/g)	Os (ng/g)	Ir (ng/g)	Pt (ng/g)
20	0.390	0.051	0.340	0.010	0.014	0.141
40	0.511	0.076	0.366	0.008	0.008	0.126
60	0.303	0.071	0.361	0.009	0.009	0.125
80	0.414	0.064	0.349	0.010	0.009	0.128

表 5　不同镍基体的铂族元素含量

Table 5　PGE contents in different Ni matrices.

试剂	Ru (ng/g)	Rh (ng/g)	Pd (ng/g)	Os (ng/g)	Ir (ng/g)	Pt (ng/g)
镍粉	0.469	0.095	0.509	4.977	1.962	0.590
硝酸镍	0.779	0.169	0.918	1.107	0.573	0.753
氧化镍	0.560	0.159	0.452	0.480	0.744	0.597
Ⅴ-羰基镍	0.175	0.109	0.096	0.050	0.006	0.120
Ⅵ-羰基镍	0.012	0.010	0.091	0.009	0.009	0.125

表 6　镍元素对钌元素测定结果的影响

Table 6　Influence of Ni on the determination results of Ru.

样品编号	Ru 的加入量 (ng/mL)	Ni 的加入量 (ng/mL)	Ru 的测定值 (ng/mL)	Ru 的回收率 (%)
1	0.04	500	0.042	105
2	0.04	1000	0.047	116
3	0.04	5000	0.053	133
4	0.04	10000	0.060	150
5	0.04	50000	0.086	214
6	0.04	100000	0.122	304
7	0.04	500000	0.209	521

2.2　溶液中镍和测定模式的影响

2.2.1　溶液中镍对铂族元素测定的影响

以丰度高和不受同量异位素干扰为原则，选择 ^{195}Pt、^{105}Pd、^{101}Ru、^{103}Rh、^{190}Os 和^{193}Ir 作为测定同位素。实际测定中发现，^{195}Pt、^{105}Pd、^{103}Rh、^{190}Os 和 ^{193}Ir 的测定相对稳定，而钌易受到多原子离子的干扰。干扰^{101}Ru 的多原子离子有：^{12}C^{89}Y、^{16}O^{85}Rb、^{16}O^{1}H^{84}Kr、^{14}N^{87}Rb、^{1}H^{100}Ru、^{1}H^{100}Mo、^{14}N^{87}Sr、^{40}Ar^{61}Ni、^{13}C^{88}Sr、^{16}O^{1}H^{84}Sr、^{36}Ar^{65}Cu。采用镍锍试金分离富集样品中铂族元素，能使其与大部分贱金属元素有效分离。但是，由于捕集剂为硫化镍，过滤时很难洗净镍离子，待测试液中残留的镍会形成一系列多原子离子：^{61}Ni^{40}Ar、^{64}Ni^{37}CI、^{64}Ni^{40}Ar 等。其中，^{61}Ni^{40}Ar 对^{101}Ru 的测定形成严重干扰。

标准模式下，测定 0.04ng/mL 钌单元素标准溶液在 0.5～500μg/mL 镍基体中的回收率，从表 6 中数据可见，当镍质量浓度低于 1μg/mL 时，钌的回收率小于 116%，此时由镍形成的多原子离子质谱干扰可忽略不计，当镍质量浓度超过 1μg/mL(镍和钌浓度比为 25000：1)，其形成的多原子离子质谱干扰越来越明显，严重影响钌的测定。

根据实验结果，发现当溶液中镍含量在 500～500000ng/mL 范围时，线性关系良好。以溶液中镍的质量浓度 (ng/mL) 为已知量，镍干扰形成的钌质量浓度 (ng/mL) 为未知量，可以得到镍元素对钌元素的干扰校正方程，见公式 (1)。

$$\rho_{\mathrm{Ru}} = 0.00007\rho_{\mathrm{Ni}}^{0.6017} \tag{1}$$

式中：ρ_{Ru}—由于镍干扰形成的钌的质量浓度 (ng/mL)；ρ_{Ni}—溶液中镍的质量浓度 (ng/mL)。

因此，采用标准模式测定钌时，当镍与钌的浓度比大于 25000：1 时，根据公式 (1) 能够基本扣除镍对钌的干扰，但当镍的浓度过大时，此消除干扰方式效果不佳。

2.2.2　标准模式和动能歧视模式测定结果的比较

在标准模式和动能歧视模式两种模式下测定 0.04ng/mL 钌单元素溶液在 0.50～500μg/mL 镍基体中的回收率，来考察不同测定模式下镍对钌测定的影响。由图 1 可知，在标准模式下，当镍质量浓度小于 5μg/mL 时，钌回收率约在 120% 以内，标准模式和动能歧视模式测定结果无明显差别；当镍质量浓度超过 10μg/mL 后，标准模式下钌回收率明显升高，说明镍所形成的^{61}Ni^{40}Ar^{+}质谱干扰较为严重。而在动能歧视模式下，镍质量浓度在 0.50～500μg/mL 范

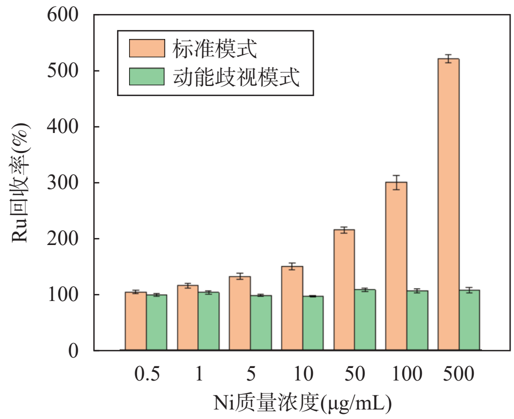

图1　两种模式下干扰元素镍对钌测定的影响

Fig. 1　Effect of interference element Ni on the determination of Ru in two modes.

围内, 钌的测定值相对稳定。

为进一步研究 ICP-MS 在动能歧视模式下消除质谱干扰的优势, 在标准模式和动能歧视模式下分别采集 500μg/mL 镍溶液中钌的信号强度进行对照试验。标准模式下钌元素背景等效浓度 (BEC) 为 0.16ng/mL, 动能歧视模式下可降至 0.0040ng/mL, 在动能歧视模式下, 钌元素的背景等效浓度比标准模式降低近 2 个数量级。综上, 实验选择动能歧视模式进行测试。

2.3　方法检出限和测定下限

根据条件实验结论, 按照实验方法进行 20 次全流程空白试验, 在仪器设定工作条件下, 使用动能歧视模式测定, 计算 20 次空白标准偏差, 取样量按 20g 计, 考虑稀释倍数, 以 3 倍空白标准偏差计算方法的检出限, 以 10 倍空白标准偏差计算方法的测定下限。钌的检出限达到 0.005ng/g(表 7), 使铂族六项元素检出限同时满足超痕量铂族元素的测定要求。

2.4　方法精密度和正确度

为了考察本文方法测定超痕量铂族元素的精密度和正确度, 选择超痕量铂族元素地球化学成分分析标准物质 (中国地质科学院地球物理地球化学勘查研究所研制), 按照实验方法对每个样品平行测定 12 次, 进行精密度试验和加标回收试验。从表 8 中数据可见, 6 个元素相对误差 (RE) 为−10.9% ~ 11.8%, 相对标准偏差 (RSD, n=12) 小于 9.37%, 加标回收率为 92% ~ 110%, 满足《地质矿产实验室测试质量管理规范》(DZ/T 0130.4—2006) 中关于 1 : 200000 分析方法的准确度和精密度控制限 (3 倍检出限内, RE ≤±23%, RSD≤17%; 大于 3 倍检出限, RE≤±12%, RSD≤10%) 及 DZ/T 0130.3—2006 中关于加标回收率允许限 (组分含量在 10^{-6} ~ 10^{-4} 时, 加标回收率 90% ~ 110%; 组分含量 > 10^{-4} 时, 加标回收率 95% ~ 105%)。

3　结论

建立了镍锍试金富集 ICP-MS 测定地质样品中的超痕量铂族元素的方法。通过试剂的筛选及采用水浸泡锍扣, 使锍扣自行粉化松散, 省略了机械碎扣步骤, 避免了污染并控制了实验过程产生的空白。同时, 采用 ICP-MS 动能歧视模式测定铂、钯、铑、铱、锇和钌, 解决了钌的质谱干扰问题, 降低了方法检出限。该方法应用于超痕量地球化学标准物质分析, 测定值与标准值一致, 适用于大批量地质样品中超痕量铂、钯、铑、铱、锇和钌的同时测定。

采用该方法分析了中国地质科学院地球物理地球化学勘查研究所承担的《东南亚及中亚地区多尺度地球化学填图及成果集成应用》等项目中铂族元素的测定, 测定结果满足相关规范要求, 成图效果良好, 为地球化学调查提供技术支撑。今后将该方法应用于地质样品分析的同时, 还需深入探索硫化镍与金的共存机理, 提高镍锍试金对金的捕集效果, 进一步增加可同时测定元素的数量。

表 7　动能歧视模式下铂族元素检出限和测定下限

Table 7　Detection limits and quantification limits for PGEs in kinetic energy discrimination model.

方法参数	Ru (ng/g)	Rh (ng/g)	Pd (ng/g)	Os (ng/g)	Ir (ng/g)	Pt (ng/g)
空白平均值	0.013	0.008	0.155	0.015	0.011	0.112
检出限 (3s)	0.005	0.008	0.050	0.012	0.007	0.058
测定下限 (10s)	0.015	0.024	0.150	0.036	0.021	0.174

表 8 标准物质分析结果

Table 8 Analytical results of PGEs in national reference materials.

标准物质编号	元素	测定值 (ng/g)	RSD (%)	标准值 (ng/g)	相对误差 (%)	加标量 (ng/g)	测定总值 (ng/g)	回收率 (%)
GBW07288 (土壤)	Ru	0.053	7.21	0.05	6.00	0.05	0.101	94
	Rh	0.019	7.31	0.017	11.8	0.05	0.068	98
	Pd	0.290	9.23	0.26	11.5	0.5	0.750	92
	Os	0.055	8.05	0.05	10.0	0.05	0.109	108
	Ir	0.035	8.55	0.032	9.38	0.05	0.081	92
	Pt	0.280	6.93	0.26	7.69	0.5	0.790	102
GBW07289 (水系沉积物)	Ru	0.110	5.38	0.1	10.0	0.1	0.220	110
	Rh	0.103	7.08	0.095	8.42	0.1	0.198	95
	Pd	2.200	7.66	2.3	−4.35	5	7.660	109
	Os	0.066	7.96	0.06	10.0	0.05	0.120	108
	Ir	0.054	7.16	0.05	8.00	0.05	0.103	98
	Pt	1.700	5.33	1.6	6.25	1	2.790	109
GBW07294 (土壤)	Ru	0.588	6.28	0.66	−10.9	0.5	1.051	93
	Rh	1.080	5.88	1.1	−1.82	1	2.010	93
	Pd	15.100	3.85	15.2	−0.66	10	25.600	105
	Os	0.650	9.37	0.64	1.56	0.5	1.170	104
	Ir	1.110	3.88	1.2	−7.50	1	2.131	102
	Pt	14.100	3.99	14.7	−4.08	10	23.500	94

Ultratrace Platinum Group Elements in Geological Samples by Inductively Coupled Plasma-Mass Spectrometry with Nickel Sulfide Fire Assay

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HIGHLIGHTS

(1) The source of the blank was identified by checking reagent blanks and the purification methods for reagents were given. Carbonyl nickel powder was used as a nickel collector, with the lower reagent blank, and the detection limits for PGEs required by geochemical exploration were achieved.

(2) Carbonyl iron powder was added to ensure the NiS bead could be smashed in deionized water. In this way, the analysis process was simplified, and the risk of contamination caused by mechanical breakage of NiS bead was avoided.

(3) Using ICP-MS to determine the solution in the kinetic energy discrimination model effectively eliminated the matrix effect of Ni. The results showed that the background equivalent concentration of ruthenium in kinetic energy discrimination mode was two orders of magnitude lower than that in the standard mode.

ABSTRACT: Pt, Pd, Rh, Ir, Os and Ru are platinum group elements (PGEs) with similar properties. Due to the low abundance as well as the nugget effect, the accurate determination of PGEs has been a challenge for rock and mineral analysis. Fire assay methods with large sample weights were developed to separate and preconcentrate PGEs, however, there are still difficulties to accurately determine ultratrace PGEs because of the high reagent blanks and the matrix effect. A method of nickel sulfide fire assay combined with ICP-MS simultaneous determination of ultratrace PGEs in samples was established. The results showed that the blank mainly comes from hydrochloric acid and nickel collector when using nickel sulfide fire assay to capture PGEs. The intensities of PGEs were detected by ICP-MS in standard mode and kinetic energy discrimination. In standard mode, the detection limits were 0.2ng/g for Pt and Pd, and 0.02ng/g for Rh, Ir and Os, but it couldn't reach 0.1ng/g for Ru. In kinetic energy discrimination, the background equivalent concentration of Ru was two orders of magnitude lower than that in the standard mode. With the matrix effect of Ni effectively eliminated, the detection limits reached 0.005ng/g for Ru. The detection limits for PGEs required by geochemical exploration were achieved. The certified reference materials of soil (GBW07288, GBW07294) and stream sediment (GBW07289) were analyzed to test the method. The determined values were in good agreement with the certified values. The relative errors were between −10.9% and 11.8%, the relative standard deviations (RSD, n=12) were 3.88%−9.37%, and the spiked recoveries were 92%−110%. This method is simple, rapid and meets the requirements of ultratrace PGEs determination in large quantities of geological samples. The BRIEF REPORT is available for this paper at http://www.ykcs.ac.cn/en/article/doi/10.15898/j.ykcs.202407180159.

KEY WORDS: nickel sulfide fire assay; inductively coupled plasma-mass spectrometry; kinetic energy discrimination model; PGEs; soil; sediment

BRIEF REPORT

Significance: Platinum-group elements (PGEs), such as Pt, Pd, Rh, Ir, Os and Ru exhibit similar physico-chemical properties and significant features, and have been used widely in geochemistry and environmental chemistry. As a result, the accurate determination of the concentration of PGEs in geological samples is very important. Although various analytical methods for PGEs have been developed in the past, accurate and simultaneous determination of PGEs concentrations on the same sample digestion remains a significant challenge. This is mainly due to: (1) their extremely low abundance, sample heterogeneity and the nugget effect, making it necessary to analyze large sample sizes to obtain representative analyses; (2) During sample dissolving, Os and Ru are easy to form volatile OsO_4 and RuO_4, making it difficult to simultaneously measure the concentrations of PGEs accurately.

Improved Carius tube combined high-pressure asher (HPA-S) techniques have been widely used for the determination of PGEs to avoid the loss of volatile OsO_4 and RuO_4. However, the relatively complex procedure does not meet the requirements of ultratrace PGEs determination in large quantities of geological samples. Nickel sulfide (NiS) fire assay is a classical method to completely extract the PGEs from a large sample size into a nickel sulphide button and easily separate it from the slag. This method combined with highly sensitivity instrumental measurement, i.e., inductively coupled plasma-mass spectrometry (ICP-MS), can be used to simultaneously determine multi-elements with high sensitivity and effectively reduce the detection limit. However, it is still difficult to determine ultratrace PGEs because of the high procedural blank that mainly derives from the commercial nickel reagents and polyatomic ion interferences formed by interaction of a sample aerosol with components of the plasma-forming gas (such as C, Ar) and residual Ni and Cu ions in solution. Therefore, the improvement of the method for simultaneous determination of PGEs by ICP-MS combined with nickel sulfide fire assay preconcentration is important.

An analytical method for accurate and simultaneous determination of ultratrace PGEs in geological samples by ICP-MS combined with nickel sulfide fire assay is proposed. At the same time, it can effectively reduce the procedural blank and suppress/eliminate interferences. More importantly, it provides a practical method for the accurate determination of ultratrace PGE concentrations on the same sample digestion for surveying a large number of geological samples.

Methods: In the experiment, it is important to reduce the procedural blank and suppress/eliminate interferences. The data show that the high reagent blank is primarily from hydrochloric acid (Table 3) and nickel collector (Table 5). Therefore, the hydrochloric acid after purification or obtained from other manufacturers can be used in the experiment. At the same time, carbonyl nickel powder rather than other type of nickel powder is used as the fire assay collector.

Before analysis, the PGEs concentrations in the reagent (including hydrochloric acid and nickel powder) were measured. The reagent was not suitable to analyze the ultratrace PGEs, when the results exceeded 0.02ng/mL. (1) 50mL hydrochloric acid was evaporated at low temperature, and 5mL of *aqua regia* prepared from the same bottle of hydrochloric acid was added. After being extracted at low temperature and adding 20mL of deionized water, the solution was determined by ICP-MS. (2) 1.6g nickel power was mixed well with 2g sulfur, 4g carbonyl iron powder, 25g $Na_2B_4O_7·10H_2O$, 25g Na_2CO_3, 4g SiO_2, and 1g of edible flour and transferred into a 500mL fire-clay crucible, and fused in a furnace at approximately 1000℃. The furnace door was opened to cool to 800℃. Then the door was closed, and temperature gradually rose to 1050℃ and maintained for 30min. The fluid in the crucible was poured into a cast iron mold. After cooling, the NiS bead was separated from the slag, and placed into a 200mL Triangle bottle with 20mL deionized water until smashed. Then 20mL concentrated HCl was added into the Triangle bottle and heated for 1h until no bubbles formed. Filtering out the sediment through a filter membrane, sediment was transferred into a 200mL Triangle bottle and 5mL *aqua regia* was added. Next the air-cooled tube was loaded, and the solution was heated to boiling. The cooling solution was diluted to 25mL by the addition of deionized water. Lu (50ng/mL) was added as an internal standard for the determination of Pt, Pd, Ru, Rh and Ir by ICP-MS (Table 1) in kinetic energy discrimination mode.

Ultratrace PGEs in geological samples were determined after the reagent blanks were checked. 20g sample was mixed well with the above-mentioned flux and collectors (proration shown in Table 2). The fusion procedure was also described above. The solution was determined by ICP-MS in kinetic energy discrimination mode, which can effectively eliminate the matrix effect.

Data and Results: Determination of ruthenium in geological samples by ICP-MS, showed that the background equivalent concentration of ruthenium in kinetic energy discrimination mode was two orders of magnitude lower than that in the standard mode (Fig.1). In kinetic energy discrimination mode, the detection limit of the method was 0.005ng/g (Table 8). The certified reference materials of soil (GBW07288, GBW07294) and stream sediment (GBW07289) were analyzed to test the method. The determined values were in good agreement with the certified values. The relative errors were between −10.9% and 11.8%, the relative standard deviations (RSD, n=12) were 3.85%−9.37%, the spiked recoveries were between 92% and 110%.

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