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## 次氯酸氧化 ICP-MS 同时测定金矿石中金和伴生元素银铜铅锌砷锑

王啸<sup>1</sup>, 刘玖芬<sup>2,3\*</sup>, 甘黎明<sup>1</sup>, 李荣华<sup>1</sup>, 王西<sup>1</sup>, 魏欣<sup>1</sup>, 何涛<sup>1</sup>

(1. 中国地质调查局西安矿产资源调查中心, 陕西 西安 710100;

2. 中国地质大学(北京), 北京 100083;

3. 中国地质调查局自然资源综合调查指挥中心, 北京 100055)

**摘要:** 金矿石是重要的战略性矿产资源, 除需检测金含量外, 还需检测银铜铅锌砷锑等伴生元素含量。由于金矿石中往往含有碳质物和硫化物, 对金的浸出有影响, 现有方法需要焙烧-消解-预富集后测定, 矿物中硫化物、氧化砷、卤化锑等化合物沸点均低于 565℃, 金矿石在 650℃ 焙烧时砷、锑极易损失, 因此银铜铅锌砷锑需单独消解测定, 极为繁琐。本文利用次氯酸的强氧化性, 在硝酸介质中氧化碳质物与硫化物替代焙烧样品, 结合离线内标建立了电感耦合等离子体质谱(ICP-MS)同时测定金银铜铅锌砷锑的方法。研究了次氯酸用量、消解时间、内标和干扰元素对分析结果的影响, 结果表明 10.0000g 样品加入 20mL 硝酸和 5mL 次氯酸于电热板沸腾溶解近干, 可将碳质物与硫化物完全氧化, 稀释因子为 1000 时金银铜铅锌砷锑的检出限分别为 0.03、0.05、0.19、0.26、0.22、0.27、0.05μg/g。应用本方法对高品位碲金矿成分分析标准物质(GBW07858、GBW07859)进行测定, 结果与标准值相符; 对 5 个不同类型的金矿石实际样品进行测定, 结果与《金矿石化学分析方法》(GB/T 20899—2019)单独测定结果相符, 各元素相对误差均≤5.32%, 相对标准偏差(RSD, n=7)≤4.71%。本方法解决了金与银铜铅锌砷锑等伴生元素无法同时测定的问题, 并省去了焙烧样品与金预富集步骤, 流程简便。

**关键词:** 次氯酸; 电感耦合等离子体质谱法; 金矿石; 金; 伴生元素

**要点:**

(1) 采用次氯酸氧化碳质物和硫化物消除对金测定的影响, 避免样品预焙烧导致砷、锑损失。

(2) 样品经消解与分液, ICP-MS 可直接测定金银铜铅锌砷锑, 省去金预富集步骤。

(3) 利用离线内标, 实现 ICP-MS 一个体系中同时测定金银铜铅锌砷锑。

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金矿是具有金融价值的战略性矿产资源, 常伴生有一定量的伴生元素银铜铅锌砷和锑, 其中砷和锑与金密切共生, 对金矿找矿具有一定指示作用, 银铜铅锌含量直接影响金矿经济价值。因此, 快速准

确测定金与银铜铅锌砷锑等伴生元素含量, 对提高金矿找矿效能具有十分重要意义<sup>[1-3]</sup>。

当前, 矿石中金的测定方法主要有原子吸收光谱法<sup>[4-10]</sup>、伏安法<sup>[11-12]</sup>、电感耦合等离子体质谱

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第一作者: 王啸, 硕士, 高级工程师, 主要从事岩石矿物分析研究。E-mail: 418804826@qq.com。

通信作者: 刘玖芬, 硕士, 正高级工程师, 主要从事地球化学和分析测试研究。E-mail: 13863858360@163.com。

法(ICP-MS)<sup>[13-15]</sup>、电感耦合等离子体发射光谱法(ICP-OES)<sup>[16]</sup>等;银、铜、铅和锌的测定方法主要有原子吸收光谱法(AAS)<sup>[17-18]</sup>、ICP-OES法<sup>[19-20]</sup>、ICP-MS法<sup>[21]</sup>等;砷和锑的测定主要有原子荧光光谱法<sup>[22]</sup>、AAS法<sup>[23-24]</sup>、ICP-MS法<sup>[25]</sup>、ICP-OES法<sup>[26-27]</sup>等。标准分析方法中,金的测定为焙烧-消解-预富集后 AAS法(GB/T 20899.1—2019),银铜铅锌砷和锑的测定为酸溶 ICP-MS法(GB/T 20899.15—2023)。现有方法金与伴生元素需全流程独立检测,无法实现金矿石中金银铜铅锌砷和锑的同时测定。金矿中金的测定易受到硫化物及碳质物的影响,通常需要焙烧消除,在湿法直接消解中,罗永红等<sup>[28]</sup>采用高锰酸钾-氯酸钾湿法氧化除碳和硫替代焙烧,结合活性炭富集,用 AAS法测定矿石中的金,该法有效地去除了硫化物及碳质物干扰,但该氧化体系增加了溶液的盐类浓度不适用于 ICP-MS测定。对于矿石中金的直接测定,葛艳梅等<sup>[29]</sup>通过焙烧-王水溶解,用 AAS法对金矿石中高品位金进行了测定;Rodriguez等<sup>[30]</sup>利用中子活化分析对墨西哥两种矿石样品中银金铜和锌进行了测定;张洁等<sup>[31]</sup>通过焙烧-王水溶解,用 ICP-MS法对金矿石中金进行了测定。以上方法实现了金矿石的湿法氧化与金元素的直接测定,但砷锑等伴生元素仍须单独消解测定。

本文利用次氯酸替代了高锰酸钾-氯酸钾湿法氧化体系,次氯酸分解产生的新生态氧具有极强的氧化性,在硝酸介质中可快速氧化样品中的碳质物与硫化物,还原产物未引入锰、钾等高盐分。以次氯酸氧化,避免样品预焙烧导致的砷、锑损失,在未增加盐分的情况下有效地消除了硫化物及碳质物对金前处理的影响,结合离线内标法,减小分液与测定仪器漂移带来的误差,建立了 ICP-MS同时测定金矿石中金和伴生元素银铜铅锌砷锑的方法。

## 1 实验部分

### 1.1 仪器和设备

7700 Series 电感耦合等离子体质谱仪(美国 Agilent 公司),主要仪器参数见表 1。

BS124S 分析天平(德国 Sartorius 公司),感量 0.01mg; D-1000 移液器(BRAND),规格为 100~1000 $\mu$ L。

### 1.2 标准溶液和主要试剂

金元素标准溶液: 100.0 $\mu$ g/mL,介质为 2.0mol/L 盐酸;多元素混合标准溶液:银、铜、铅、锌、砷、锑

表 1 电感耦合等离子体质谱分析工作条件

Table 1 The instrument parameters of ICP-MS.

工作参数	设定值	工作参数	设定值
ICP 射频功率	1550W	Omega 透镜	10V
载气流速	0.7L/min	反应池入口	-30V
雾室温度	2 $^{\circ}$ C	反应池出口	-50V
采样深度	7mm	偏转电压	10V
提取透镜 1	0V	泵速	30r/min
提取透镜 2	-140V	雾化器气体流速	0.80L/min
Omega 偏置电压	-80V	氧化物产率	0.67%

元素的质量浓度均为 10.00 $\mu$ g/mL,介质为 1.0mol/L 硝酸;铊标准溶液: 10.00 $\mu$ g/mL,介质为 2.0mol/L 盐酸;铕标准溶液: 10.00 $\mu$ g/mL,介质为 1.0mol/L 硝酸,均购自国家有色金属及电子材料分析测试中心;活性炭: 优级纯,石墨碳: 优级纯,均购自国药集团化学试剂有限公司。

调谐液: 铈、钴、锂、镁、铈、钇质量浓度均为 1.00ng/mL,购自美国 Agilent 公司。

硝酸(1.42g/mL)、盐酸(1.18g/mL)、次氯酸(1.00mg/mL): 均为分析纯,购自成都市科隆化学品有限公司。

### 1.3 校准曲线

金标准溶液系列: 准确量取一定体积的金标准储备溶液,用体积分数为 3% 王水溶液逐级稀释,配制成金质量浓度依次为 0、0.10、0.50、1.00、2.00、5.00、10.0、20.0ng/mL 的溶液,同时在金标准溶液系列中加入铊,控制铊的质量浓度为 10.0ng/mL。

银铜铅锌砷锑标准溶液系列: 准确量取一定体积的多元素混合标准溶液,用体积分数为 3% 王水溶液逐级稀释,配制成银、铜、铅、锌、砷、锑的质量浓度均分别为 0、1.00、5.00、10.0、50.0、100、500、1000、2000 $\mu$ g/L 的系列混合标准工作溶液,同时在混合标准工作溶液系列中加入铊,控制铊的质量浓度为 100ng/mL。

### 1.4 实验样品

选取包含金、银、铜、铅、锌、砷和锑定值的高品位砷金矿成分分析国家一级标准物质 GBW07858、GBW07859(黑龙江省地质矿产测试应用研究所研制)和实际样品作为实验样品(编号: S1、S2、S3、S4、S5,粒度 $\leq$ 0.074 $\mu$ m,由陕西凤县四方金矿有限公司提供)。

由于国家一级标准物质中的硫、碳、铜、铅、锌、砷、锑含量较低,因此选用硫、碳与待测元素含量均较高的 S5 实际样品(硫含量 11.45%,总碳含量 6.85%,有机碳含量 1.26%)作为实验条件优化样品,

国家一级标准物质 GBW07858、GBW07859 和实际样品均作为准确度和精密密度验证样品。

### 1.5 样品分析方法

①准确称取 10.0000g 样品于 300mL 聚四氟乙烯烧杯中,用水润湿,依次加入 20mL 硝酸、5mL 次氯酸、3.0g 氟化氢铵、1.00mL 质量浓度为 10.00 $\mu$ g/mL 的铈内标溶液和 10.00mL 质量浓度为 10.00 $\mu$ g/mL 的铈内标溶液,盖上表面皿,置于电热板上加热,保持微沸状态 10min。②观察溶液表面是否漂浮一薄层黑色碳膜,如无则补加 1.00mL 次氯酸,加热至近干;如有黑色碳膜则补加 1.00mL 次氯酸,加热 5min,直至黑色碳膜消失,再补加 1.00mL 次氯酸,加热至近干。③用 80mL 50% 王水溶液复溶,微沸溶解 50min 后取下烧杯,用温热水冲洗表面皿及杯壁,冷却后转移至 200mL 容量瓶中,定容后充分摇匀。④用移液器分取 500 $\mu$ L 样品溶液以 2% 王水溶液稀释 50 倍(样品稀释因子为 1000),摇匀后以 ICP-MS 测定。本文中样品稀释因子的计算公式为:样品稀释因子=样品溶液的液固比(g/mL) $\times$ 样品溶液的稀释倍数。

## 2 结果与讨论

### 2.1 实验条件的选择

#### 2.1.1 次氯酸用量与氧化时间的关系

次氯酸分解产生的新生态氧具有极强的氧化性,分解反应方程式见(1),硝酸亦具有氧化性,硝酸中加入次氯酸可快速地氧化样品中的碳质物与硫化物。



碳质物(单质碳和有机碳)和硫化物常存在于样品中,其中单质碳多为晶质石墨和非晶质木炭及炭黑,有机碳则以植物残枝和腐植质为主。这些含碳物质极易吸附 Au(III),对金的测定有影响,植物残枝和腐植质等有机碳对 Au(III)的吸附能力较弱,而单质碳(晶质石墨和非晶质木炭等)对 Au(III)的吸附能力很强;样品溶液中存在的硫离子易生成硫化物包裹 Au(III),同样影响金的测定<sup>[30]</sup>。由于碳的电负性较高,束缚电子的能力较强,相比于硫离子更难被氧化,因此选用吸附金能力强且难被氧化的活性炭和石墨碳开展次氯酸氧化条件试验。

准确称取 0.05g 活性炭和石墨碳各 4 份,分别置于 4 个烧杯中,加入 3.0、4.0、5.0、6.0mL 次氯酸和 20mL 硝酸,置于电热板上加热,溶液微沸时开始计时,以液面中黑色碳膜完全消除停止计时,所耗时间为氧化时间。由实验结果(表 2)可以看出,5mL

次氯酸在 5min 内能将 0.05g 活性炭完全氧化,而对于 0.05g 石墨,5mL 次氯酸需 10min 能将其完全氧化。因此,针对金矿石中的碳物质,以加入 5mL 次氯酸为宜。溶样过程中,如液面漂浮一薄层黑色碳膜,应补加次氯酸,加热至黑色碳膜消失为止。

准确称取 0.05g 活性炭和石墨碳,分别加入 1.00mL 质量浓度为 5 $\mu$ g/mL 金、银标准溶液,加入 5mL 次氯酸和 20mL 硝酸,按照实验方法进行全流程分析测定。金、银加标回收率在 97.0%~103.0% 之间(表 3),说明碳物质氧化完全,未吸附金、银。

表 2 次氯酸用量与氧化时间关系

Table 2 The relationship between the dosage of hypochlorous acid and oxidation time.

样品名称	次氯酸用量 (mL)	完全氧化时间 (min)
活性炭	3	11
	4	8
	5	5
	6	4
石墨	3	19
	4	16
	5	10
	6	9

表 3 金和银加入标准回收试验

Table 3 The recovery tests of Au and Ag.

样品名称	元素	加标量 ( $\mu$ g/g)	测得总量 ( $\mu$ g/g)	回收率 (%)
活性炭	Au	5.00	4.98	97.0
	Ag	5.00	4.94	103.0
石墨	Au	5.00	5.02	97.4
	Ag	5.00	4.97	100.5

#### 2.1.2 氟化氢铵的用量

金矿石易包裹在石英脉中,少量金、银可能会被硅酸盐包裹,加入氟化氢铵可分解产生氢氟酸,消解硅酸盐包裹的金与银。称取编号为 S5 的样品 10.0000g 各 5 份,分别加入 0.0、1.0、2.0、3.0、4.0g 氟化氢铵按实验方法测定金和银。由实验结果(图 1)可以看出,加入氟化氢铵对金的测定结果基本没有影响,金常以裸露单质形式存在,硅酸盐包裹金很少,可忽略不计。而对于银,随着氟化氢铵加入量的增加,银的测定结果略有升高,当氟化氢铵加入量大于 2.0g 时银的测定结果趋于稳定,可将硅酸盐包裹的少量银消解。故选择加入 3.0g 氟化氢铵为最佳用量。

#### 2.1.3 溶解时间

样品溶解时间对金、银、铜、铅、锌、砷和铋的

溶解率均有影响,增加溶解时间有助于各元素溶解完全。称取编号为 S5 的样品 10.0000g,经次氯酸-氟化氢铵-硝酸体系消解近干后,加入 60mL 50% 王水分别在 20、30、40、50、60min 时间下复溶,按实验方法测定金、银、铜、铅、锌、砷和锑。由实验结果(图2)

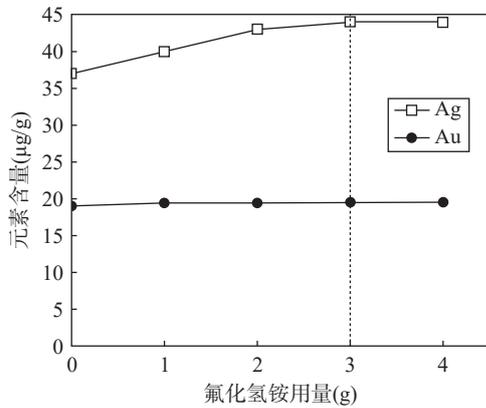


图1 氟化氢铵用量对金和银测定结果的影响

Fig. 1 The influence of ammonium bifluoride dosage on determination of Au and Ag.

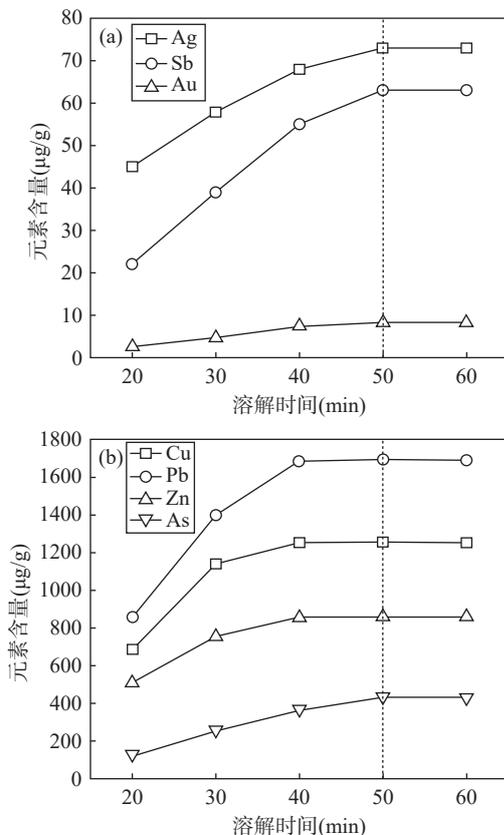


图2 溶样时间对金、银、锑、铜、铅、锌和砷测定结果的影响

Fig. 2 The influence of sample dissolution time on determination of Au, Ag, Sb, Cu, Pb, Zn and As.

可以看出,随复溶时间延长,本法测定值逐步趋于稳定;溶样大于 40min 时铜、铅和锌的测定结果基本不变,溶样 50min 时金、银、砷和锑的测定结果基本不变。故选用最佳溶样时间为 50min。

## 2.2 ICP-MS 测定金银铜铅砷锑

### 2.2.1 内标的选择

#### (1) 内标方式

由于该方法的称样量较大,样品消解后盐类浓度大,同时为兼顾金、银、铜、铅、锌、砷和锑同时测定,样品溶液稀释 50 倍(稀释因子为 1000)再采用 ICP-MS 测定,可能产生误差,因此实验中采用离线内标法来避免样品稀释与仪器波动引起的误差,离线内标法测定方式见 1.5 节样品分析方法所述。

#### (2) 内标浓度

金矿石中金的质量浓度基本低于  $20\mu\text{g/g}$ , 样品稀释因子为 1000 时,稀释后待测溶液中金的质量浓度一般低于  $20\text{ng/mL}$ ,以内标浓度与待测物浓度相近为原则,选用  $10\text{ng/mL}$  铯用于金的离线内标校正,即样品消解前加入  $1.0\text{mL}$  质量浓度为  $10\mu\text{g/mL}$  的铯内标溶液。由于其他伴生元素的质量浓度相对较高,因此选用  $100\text{ng/mL}$  铊用于银、铜、铅、锌、砷和锑的离线内标校正,即样品消解前加入  $10\text{mL}$  质量浓度为  $10\mu\text{g/mL}$  的铊内标溶液。

### 2.2.2 干扰元素

在样品测定前通过调谐雾化气流速,使仪器的氧化物产率  $I_{\text{CeO}^+/\text{Ce}} < 3\%$  以减少多原子氧化物的干扰。钽和铪的质量浓度不高于  $100\text{ng/mL}$  时,其不干扰  $^{197}\text{Au}$  的测定<sup>[30]</sup>,金矿石中钽和铪基本的质量浓度均低于  $10\mu\text{g/g}$ ,测定液中共存的钽和铪质量浓度均低于  $10\text{ng/mL}$ ,因此钽和铪对金的测定干扰可忽略。 $^{107}\text{Ag}$  的测定通过干扰系数消除  $^{91}\text{Zr}^{16}\text{O}$ 、 $^{90}\text{Zr}^{17}\text{O}$  等复合离子干扰; $^{75}\text{As}$  的测定通过干扰系数消除  $^{40}\text{Ar}^{35}\text{Cl}$  等多原子复合物干扰<sup>[31-32]</sup>;金矿石中铜、铅、锌和锑相较于化探样品含量较高,且不易形成质谱干扰,未作考量。

## 2.3 方法检出限和测定范围

按照实验方法分别制备 11 份样品空白,用 ICP-MS 进行测定,计算各元素样品空白标准偏差,采用 3 倍标准偏差计算得出各元素方法的检出限,以 4 倍的检出限计算各元素测定下限,得出测定范围。金元素的检出限低至  $0.024\mu\text{g/g}$ ,银、铜、铅、锌、砷和锑等伴生元素的检出限均  $\leq 0.267\mu\text{g/g}$ (表 4)。各元素检出限、测定范围均满足一般金矿石中金与伴生元素的测定需求。

表 4 各元素检出限和测定范围

Table 4 Detection limits and measurement ranges of each element.

元素	空白测定值 ( $\mu\text{g/g}$ )											标准偏差 ( $\mu\text{g/g}$ )	检出限 ( $\mu\text{g/g}$ )	测定范围 ( $\mu\text{g/g}$ )
<sup>197</sup> Au	0.03	0.02	0.03	0.02	0.01	0.03	0.03	0.03	0.04	0.03	0.03	0.008	0.03	0.12 ~ 20
<sup>107</sup> Ag	0.09	0.08	0.05	0.04	0.04	0.05	0.06	0.07	0.05	0.06	0.06	0.016	0.05	0.20 ~ 1000
<sup>63</sup> Cu	0.35	0.36	0.41	0.37	0.42	0.31	0.45	0.41	0.46	0.53	0.45	0.062	0.19	0.76 ~ 2000
<sup>208</sup> Pb	0.42	0.41	0.51	0.42	0.53	0.36	0.58	0.51	0.48	0.62	0.61	0.086	0.26	1.04 ~ 2000
<sup>66</sup> Zn	0.47	0.49	0.53	0.42	0.51	0.65	0.57	0.55	0.54	0.58	0.66	0.072	0.22	0.88 ~ 2000
<sup>75</sup> As	0.52	0.54	0.61	0.55	0.63	0.46	0.67	0.51	0.59	0.76	0.48	0.089	0.27	1.08 ~ 2000
<sup>121</sup> Sb	0.11	0.12	0.10	0.14	0.09	0.10	0.12	0.11	0.10	0.12	0.11	0.014	0.05	0.20 ~ 2000

### 2.4 方法精密度和准确度

按照实验方法,对高品位碲金矿成分分析国家一级标准物质 GBW07858、GBW07859 进行 7 次平行测定,标准物质的测定结果与标准值相符,各元素相对误差均 $\leq 3.57\%$ (表 5)。

采用本方法和《金矿石化学分析方法》(GB/T 20899—2019)对实际样品(S1、S2、S3、S4、S5)进行方法对照实验( $n=7$ ),各元素测得结果的相对标准偏差(RSD,  $n=7$ )均 $\leq 4.71\%$ ,两种方法测定结果吻合,各元素相对误差均 $\leq 5.32\%$ (表 6),满足《地质矿产实验室测试质量管理规范》(DZ/T 0130—2006)要求。

### 3 结论

采用次氯酸氧化金矿中的碳质物与硫化物,替

代焙烧样品,避免了砷、锑焙烧损失,结合离线内标法,建立了次氯酸辅助消解 ICP-MS 法同时测定金矿石中金和银、铜、铅、锌、砷和锑等伴生元素的方法。本方法在有效地氧化样品中碳质物和硫化物的同时未增加样品溶液盐分,提高了 ICP-MS 测定结果准确性,可以满足矿石中金和以上伴生元素的分析要求。

本方法实现了金矿中金与伴生元素银、铜、铅、锌、砷、锑的同时直接测定,分析流程简便,无需焙烧样品与预富集金,操作过程省时,省钱,省力。不足之处是铜、铅、锌、砷和锑的测定上限不够高,当其含量高于  $2000\mu\text{g/g}$  时采用 ICP-MS 测定则需增加稀释倍数,但稀释倍数过大可能会引起测定结果误差增大。对于此情况,采用 ICP-OES 测定该样品溶液较为可靠。

表 5 标准物质测定结果

Table 5 Determination results of national standard materials.

标准物质 编号	元素	本法测定值 ( $\mu\text{g/g}$ )								RSD (%)	标准值 ( $\mu\text{g/g}$ )	相对误差 (%)
		7 次平行测定值							平均值			
GBW07858	Au	19.1	19.3	19.4	19.2	19.4	19.6	19.2	19.3	0.87	19.6 $\pm$ 0.4	1.53
	Ag	44.0	44.1	44.8	43.5	44.2	44.8	44.1	44.2	1.04	44.2 $\pm$ 1.4	0.00
	Cu	53.4	52.3	53.2	53.5	54.1	54.5	53.2	53.5	1.32	53.4 $\pm$ 3.6	0.19
	Pb	68.7	70.1	70.5	71.1	69.2	69.1	71.6	70.0	1.56	70.3 $\pm$ 2.8	0.43
	Zn	96.3	97.2	97.8	99.2	100	98.5	101	98.6	1.66	99 $\pm$ 4	0.40
	As	12.2	12.3	12.4	12.3	12.6	12.5	12.3	12.4	1.12	12.5 $\pm$ 0.8	0.80
	Sb	3.35	3.33	3.25	3.26	3.41	3.38	3.34	3.33	1.76	3.35 $\pm$ 0.28	0.60
GBW07859	Au	31.2	30.4	32.1	32.2	31.5	31.5	32.1	31.6	2.03	32.1 $\pm$ 0.7	1.56
	Ag	67.6	67.4	68.5	67.5	67.6	68.5	67.4	67.8	0.73	67.4 $\pm$ 2.8	0.59
	Cu	65.1	66.7	65.8	64.2	65.9	66.4	67.8	66.0	1.75	65 $\pm$ 4.4	1.54
	Pb	87.6	86.4	85.8	87.6	86.9	87.2	86.2	86.8	0.81	87.8 $\pm$ 3.9	1.14
	Zn	114	115	116	118	119	111	117	116	2.33	112 $\pm$ 6	3.57
	As	12.3	12.5	12.6	12.5	12.3	12.1	12.2	12.4	1.47	12.1 $\pm$ 0.8	2.48
	Sb	4.32	4.33	4.44	4.31	4.36	4.34	4.46	4.37	1.37	4.38 $\pm$ 0.34	0.23

表6 本文方法与国家标准分析方法比对实验结果

Table 6 Determination results of proposed method in this study and national standard method.

实际样品编号	元素	本法测定值 (μg/g)							RSD (%)	国标法测定均值 (μg/g)	相对误差* (%)	
		7次平行测定值						平均值				
S1	Au	0.22	0.21	0.22	0.22	0.24	0.21	0.22	0.22	4.55	0.23	4.44
	Ag	5.41	5.53	5.29	5.35	5.26	5.13	5.05	5.29	3.08	5.41	2.27
	Cu	123	125	131	133	128	124	130	128	2.99	123	3.76
	Pb	266	261	262	269	256	263	271	264	1.93	271	2.62
	Zn	87.4	83.6	87.4	85.6	88.6	85.4	90.9	87.0	2.74	85.0	2.33
	As	33.6	34.5	34.1	33.2	32.4	34.6	34.4	33.8	2.39	34.5	1.97
	Sb	11.2	10.8	11.3	10.6	11.5	11.3	10.8	11.1	3.03	10.7	3.41
S2	Au	17.9	18.1	18.5	17.7	17.9	18.4	18.6	18.2	1.90	18.3	0.78
	Ag	10.7	10.0	9.79	10.3	10.50	10.2	10.1	10.2	3.01	10.7	4.53
	Cu	541	540	539	544	551	547	542	543	0.79	538	1.00
	Pb	43.6	43.0	42.2	41.3	40.5	39.7	39.9	41.5	3.70	43.5	4.82
	Zn	121	115	124	126	116	119	128	121	4.09	115	5.32
	As	52.6	53.6	53.3	55.1	50.5	54.3	56.2	53.7	3.42	53.1	1.04
	Sb	127	123	128	119	127	131	125	126	3.07	122	3.00
S3	Au	1.12	1.07	1.16	1.18	1.11	1.15	1.07	1.12	3.84	1.15	2.39
	Ag	10.1	10.4	10.6	10.4	10.2	9.87	9.95	10.2	2.59	10.1	1.15
	Cu	93.2	93.6	96.2	95.4	97.8	97.1	94.6	95.4	1.82	94.2	1.28
	Pb	682	688	699	693	682	687	693	689	0.91	696	0.99
	Zn	243	245	241	235	247	238	248	242	1.96	241	0.59
	As	12.9	12.3	12.8	13.6	13.4	14.2	13.5	13.2	4.71	12.7	4.19
	Sb	2.31	2.19	2.26	2.48	2.23	2.31	2.37	2.31	4.18	2.39	3.53
S4	Au	3.30	3.25	3.24	3.40	3.27	3.34	3.42	3.32	2.16	3.30	0.52
	Ag	115	119	115	119	121	123	124	119	2.97	115	3.78
	Cu	104	109	105	111	112	106	107	108	2.82	107	0.67
	Pb	524	513	516	519	515	525	513	518	0.96	511	1.33
	Zn	206	204	201	199	208	207	205	204	1.59	201	1.62
	As	1163	1152	1181	1133	1154	1151	1153	1155	1.25	1147	0.72
	Sb	949	955	957	948	955	957	964	955	0.56	945	1.05
S5	Au	8.40	8.41	8.65	8.34	8.40	8.51	8.47	8.45	1.21	8.42	0.41
	Ag	65.6	67.1	65.5	64.2	63.5	65.8	65.1	65.3	1.78	65.1	0.24
	Cu	1269	1253	1256	1264	1261	1269	1252	1261	0.57	1250	0.84
	Pb	1690	1675	1681	1672	1695	1677	1680	1681	0.49	1685	0.21
	Zn	855	843	865	851	859	864	854	856	0.90	854	0.22
	As	438	423	426	435	432	437	433	432	1.30	430	0.46
	Sb	71.1	71.6	73.4	70.8	73.5	72.8	74.2	72.5	1.82	72.1	0.53

注：“\*”代表该相对误差的计算是以国标法测定平均值为真实值。

## Simultaneous Determination of Au and Associated Elements Ag, Cu, Pb, Zn, As and Sb in Gold Ore by ICP-MS with Hypochloric Acid Oxidation

WANG Xiao<sup>1</sup>, LIU Jiufen<sup>2,3\*</sup>, GAN Liming<sup>1</sup>, LI Ronghua<sup>1</sup>, WANG Xi<sup>1</sup>, WEI Xin<sup>1</sup>, HE Tao<sup>1</sup>

(1. Xi'an Center of Mineral Resources Survey, China Geological Survey, Xi'an 710100, China;

2. China University of Geosciences (Beijing), Beijing 100083, China;

3. Command Center for Natural Resources Comprehensive Survey, China Geological Survey, Beijing 100055, China)

## HIGHLIGHTS

- (1) Hypochlorous acid was used to oxidize carbonaceous materials and sulfides to avoid arsenic and antimony losses caused by sample roasting.
- (2) After digestion and separation, samples can be directly determined without the step of gold pre-enrichment.
- (3) Offline internal standards were used to achieve simultaneous determination of gold, silver, copper, lead, zinc, arsenic, and antimony in a system by ICP-MS.

**ABSTRACT:** Gold ore contains a certain amount of gold, silver, copper, lead, zinc, arsenic, and antimony. Gold needs to be determined after roasting, digestion and enrichment; arsenic and antimony are lost after roasting, while silver, copper, lead, zinc, arsenic and antimony need to be separately determined, which is extremely cumbersome. The experiment utilized the oxidizing properties of hypochlorous acid to oxidize carbonaceous materials and sulfides in a nitric acid medium instead of sample roasting. Combined with offline internal standards, a method was established for the simultaneous determination of gold, silver, copper, lead, zinc, arsenic, and antimony by ICP-MS. The amount of hypochlorous acid, digestion time, internal standard selection, and interfering elements were optimized. The results showed that the carbonaceous and sulfides materials were oxidized under the conditions of 10.0000g of the sample, 20mL of nitric acid and 5mL of hypochlorous acid with using a heating plate to deal with them until near-dryness. According to the experimental method, gold, silver, copper, lead, zinc, arsenic, and antimony were determined in five different types of gold ore samples, the results were consistent with the national standard method, and the relative standard deviations (RSDs,  $n=7$ ) were less than 4.71%. This method solves the problem of simultaneous determination of gold, silver, copper, lead, zinc, arsenic and antimony, which is simple and convenient. The BRIEF REPORT is available for this paper at <http://www.ykcs.ac.cn/en/article/doi/10.15898/j.ykcs.202403130044>.

**KEY WORDS:** hypochloric acid; inductively coupled plasma-mass spectrometry; gold ore; gold; associated elements

## BRIEF REPORT

**Significance:** Gold mines are strategic mineral resources with financial value, while also containing Ag, Cu, Pb, Zn, As and Sb. Among them, As and Sb are closely associated with Au and have a certain indicative effect on gold exploration. The content of Ag, Cu, Zn and As directly affects the economic value of gold mines. Therefore, rapid and accurate determination of them is of great significance for improving the efficiency of gold exploration<sup>[1-3]</sup>. Luo et al<sup>[28]</sup> used potassium permanganate-potassium chlorate wet oxidation to oxidize carbonaceous materials and sulfides instead of roasting, combined with activated carbon enrichment, and determined Au in ores by AAS. This method effectively removed carbonaceous material and sulfide interference, but the oxidation system increased the salt concentration of the solution and was not suitable for ICP-MS determination. For the direct determination of Au in ore, Ge et al<sup>[29]</sup> used the AAS method to determine high-grade Au in gold ore by roasting and *aqua regia* dissolution; Rodriguez et al<sup>[30]</sup> used neutron activation analysis to determine Au, Ag, Cu and Zn in two ore samples from Mexico. The existing methods require independent detection of Au and associated elements such as As and Sb throughout the entire process, which makes it extremely cumbersome to determine Au, Ag, Cu, Pb, Zn, As and Sb in gold ore.

This investigation used hypochlorous acid instead of potassium permanganate-potassium chlorate wet oxidation system. These reduction products do not introduce a high content of salt such as manganese and potassium. Oxidation with hypochlorous acid avoids the loss of arsenic and antimony caused by sample roasting, effectively eliminating the influence of carbonaceous material and sulfides on gold pretreatment without increasing salt content.

Combined with the offline internal standard method, the error caused by liquid separation and instrument drift is reduced. A method for simultaneous determination of Au, Ag, Cu, Pb, Zn, As and Sb in gold ore by ICP-MS was established, which solved the problem of the inability to simultaneously determine gold and associated elements such as As and Sb.

**Methods: (1) Experimental Samples.** Select Chinese standard substances (GBW07858, GBW07859, developed by Heilongjiang Institute of Geological and Mineral Testing and Application) and actual samples (No.S1 S2, S3, S4, S5, Particle size  $\leq 0.074\mu\text{m}$ , provided by Shaanxi Fengxian Sifang Gold Mine Co., Ltd.) as experimental samples for experimental condition optimization, accuracy and precision verification.

**(2) Instruments and Reagents.** Select 7700 series inductively coupled plasma-mass spectrometer (Agilent, USA) used for the determination of Au, Ag, Cu, Pb, Zn, As and Sb, the main instrument parameters are shown in Table 1. Select nitric acid (1.42g/mL), hydrochloric acid (1.18g/mL), and hypochlorous acid (1.00mg/mL) used for sample digestion (analytical grade, purchased from Chengdu Cologne Chemical Co., Ltd).

**(3) Experimental Methods.** (1) Accurately weigh 10.0000g of the sample into a 300mL polytetrafluoroethylene beaker, add a small amount of water, and add 20mL of nitric acid, 5mL of hypochlorous acid, 3.0g of ammonium hydrogen fluoride, 1.00mL of rhenium internal standard solution with a mass concentration of  $10\mu\text{g/mL}$ , and 10.00mL of rhodium internal standard solution with a mass concentration of  $10\mu\text{g/mL}$  in sequence. Cover the beaker with a surface dish, heat it on an electric heating plate, and maintain a slight boiling state for 10min. (2) Observe if there is a thin layer of black carbon film floating on the surface of the solution. If not, add 1.00mL of hypochlorous acid and heat to near dryness. Add 1.00mL of hypochlorous acid and heat for 5min until the black carbon film disappears. Then add 1.00mL of hypochlorous acid and heat until almost dry. (3) Dissolve in 80mL of 50% *aqua regia* solution, gently boil for 50min, then remove from the beaker. Rinse the measuring dish and cup wall with warm water, cool down, and transfer into a 200mL volumetric flask. (4) Take 500 $\mu\text{L}$  of sample solution with a pipette and dilute it 50 times with 2% *aqua regia* solution (sample dilution factor is 1000) and measure by ICP-MS. The formula for calculating the dilution factor of the sample in this paper is: sample dilution factor=liquid-solid ratio of the sample solution (g/mL) $\times$ dilution factor of the sample solution.

**(4) Quality Control.** The detection limit of the method was determined by measuring 11 blank samples, calculating the standard deviation of each element sample blank, and using 3 times the standard deviation to calculate the detection limit of each element. The accuracy evaluation of the measurement results was carried out by measuring Chinese national standard substances and calculating the relative error. The precision evaluation was conducted by independently measuring 7 actual samples, calculating the relative standard deviation, and evaluating the stability of the results.

**Data and Results:** The effects of hypochlorous acid dosage, digestion time, internal standard, and interfering elements on the analysis results were studied. The results showed that when 10.0000g of the sample was weighed, 20mL of nitric acid and 5mL of hypochlorous acid were added, and after heating, the carbonaceous material and sulfides were almost completely oxidized. Subsequently, 80mL of a 50% *aqua regia* solution was added and heated for 50min to ensure complete dissolution of the target elements in the sample residue. The detection limits for Au, Ag, Cu, Pb, Zn, As and Sb were 0.03, 0.05, 0.19, 0.26, 0.22, 0.27, and  $0.05\mu\text{g/g}$ , respectively, with the determination ranges 0.12–20, 0.20–1000, 0.76–2000, 1.04–2000, 0.88–2000, 1.08–2000, and 0.20–2000 $\mu\text{g/g}$  (Table 4). This method was applied to conduct 7 parallel measurements of the Chinese national standard substances (GBW07858, GBW07859), the results were consistent with the recommended values (Table 5); analytical results of five different types of gold ores were consistent with the petrochemical analysis of gold mines (GB/T 20899—2019), with the relative errors of each element  $\leq 5.32\%$  (Table 6).



This method used hypochlorous acid to oxidize carbonaceous material and sulfides. Compared with the potassium permanganate-potassium chlorate wet oxidation system, the nascent oxygen produced by the decomposition of hypochlorous acid has extremely strong oxidizing properties, the decomposition equation of hypochlorous acid is shown in equation (1), which avoided high content of salt such as Mg and K. Compared with the previous method of directly determining Au, the simultaneous determination of Au and associated elements such as Ag, Cu, Pb, Zn, As and Sb were determined. The operation process is time-saving, cost-effective, and labor-saving. The drawback is that the upper limit for the determination of Cu, Pb, Zn, As and Sb is not high enough. When their content is higher than 2000 $\mu\text{g/g}$ , the dilution factor needs to be increased or the sample solution determined by ICP-OES. When the dilution factor is too large, the error of the determination result may increase, so the determination of ICP-OES is more reliable in this case.

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