

SN

中华人民共和国出入境检验检疫行业标准

SN/T 0750—1999

进出口碳钢、低合金钢中铝、砷、铬、 钴、铜、磷、锰、钼、镍、硅、锡、钛、钒 含量的测定—电感耦合等离子体 原子发射光谱 (ICP—AES) 法

Import and export carbon steel and low alloyed steel—
Determination of aluminium, arsenic, chromium, cobalt, copper,
phosphorus, manganese, molybdenum, nickel, silicon, tin,
titanium, and vanadium content—Inductively coupled
plasma atomic emission spectrometric method

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质量监督检测中心

前 言

本标准是根据 GB/T 1.1—1993《标准化工作导则 第 1 单元:标准起草与表述规则 第 1 部分:标准编写的基本规定》的要求进行编写的。本标准遵守 GB/T 1.2—1996、GB/T 1.4—1998、GB/T 1467—1978 和 GB/T 10725—1989 各项规定。

制定本标准,根据不同牌号碳钢、低合金钢中不同元素含量确定本标准的测定范围。

本标准的附录 A、附录 B、附录 C 都是提示的附录。

本标准由中华人民共和国国家出入境检验检疫局提出。

本标准主要起草单位:中国进出口商品检验技术研究所。

参加本标准研制的单位:中国进出口商品检验技术研究所、厦门商检局、天津商检局、广东商检局、广西商检局、辽宁商检局、湖南商检局、上海商检局、江苏商检局、江西商检局。

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宁波市镇海区质量技术监督检测中心

中华人民共和国出入境检验检疫行业标准

进出口碳钢、低合金钢中铝、砷、铬、 钴、铜、磷、锰、钼、镍、硅、锡、钛、钒 含量的测定—电感耦合等离子体 原子发射光谱(ICP—AES)法

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1 范围

本标准规定了电感耦合等离子体—原子发射光谱法(以下简称 ICP—AES)测定碳钢,低合金钢中铝、砷、铬、钴、铜、磷、锰、钼、镍、硅、锡、钛、钒等 13 种元素,测定范围见表 1。

表 1 13 种元素的测定范围 % (m/m)

元素测定范围	Al(s)* 0.01 ~ 0.50	As 0.005 ~ 0.10	Co 0.005 ~ 0.01	Cr 0.01 ~ 1.0	Cu 0.01 ~ 0.5
元素测定范围	P 0.01 ~ 0.05	Mn 0.01 ~ 1.5	Mo 0.01 ~ 0.5	Ni 0.01 ~ 0.1	Si 0.05 ~ 0.5
元素测定范围	Sn 0.005 ~ 0.1	Ti 0.01 ~ 0.50	V 0.005 ~ 0.5		

(s)* 表示酸溶铝。

2 引用标准

下列标准所包含的条文,通过在本标准中引用而构成为本标准的条文。本标准出版时,所示版本均为有效。所有标准都会被修订,使用本标准的各方应探讨使用下列标准最新版本的可能性。

GB/T 6682—1992 分析实验室用水规格和试验方法

GB 10725—1989 化学试剂 电感耦合高频等离子体原子发射光谱法通则

JJG 015—1996 电感耦合等离子体原子发射光谱仪检定规程

GB/T 6379—1986 测试方法的精密度 通过实验室间试验确定标准测试方法的重复性和再现性

3 方法提要

试样以硝酸-盐酸溶解并稀释至确定的体积后,将试样溶液喷入等离子体焰中,并以此做光源,在等离子体光谱仪相应元素波长处,测量其光谱强度。

4 试剂和溶液

除特别声明外,本方法所用的试剂均为优级纯试剂,试验用水为去离子水均符合 GB/T 6682 的规定。

4.1 高纯铁(铁含量 > 99.98%)。

4.2 盐酸(ρ 1.19 g/mL)。

4.3 硝酸(ρ 1.42 g/mL)。

4.4 盐酸(1+1)。

4.5 盐酸(1+11)。

4.6 硝酸(1+5)。

4.7 铁基体溶液:称取 5.000 0 g 高纯铁(4.1)于 250 mL 烧杯中,加入 40 mL 盐酸(4.4),盖上表面皿,低温溶解,冷却至室温。用少量水冲洗表面皿,移入 100 mL 容量瓶中,以去离子水稀至刻度,混匀备用。此溶液为 1 mL 含 50 mg 铁。

4.8 标准溶液

4.8.1 13 种单元素标准溶液:单元素标准溶液可向国家认可的销售标准物质单位购买,其质量浓度为 1 000 mg/L(或 500 mg/L)。

4.8.2 多元素标准溶液(2 倍 N5):此溶液用单元素标准溶液(4.8.1)按表 2 计算,即分别算出相当于 2 倍 N5 的单元素标准溶液体积。按算得的体积分取 13 种元素单元素标准溶液(4.8.1)于 200 mL 容量瓶中,混匀后,用盐酸(4.5)稀至 200 mL,制成多元素标准溶液(2 倍 N5),备用。

在配制的过程中,为防止 Sn 的水解和 Si 的析出。盐酸酸度应保持在 1 mol/L 左右。

具体配置步骤参见附录表 C1。

4.8.3 标准系列溶液(N0~N6):分取 10 mL 的 Fe 基体溶液(4.7)于七个 100 mL 容量瓶中,按表 2 计算体积,分取计算量的 2 倍 N5 多元素标准溶液(4.8.2)于其中 3 个容量瓶中,并以盐酸(4.5)稀至刻度,制成标准系列 N3 至 N5 点。然后分取计算量的 N4 标准溶液于其中另 2 个容量瓶中,并以盐酸(4.5)稀至刻度制成 N1~N2 点。取铬、锰单元素标准溶液(4.8.1)各 10 mL 和硅 12 mL 于第六个 100 mL 容量瓶中,并以盐酸(4.5)稀至刻度,制成标准系列 N6 点。第七个为 N0 点。

在 N0 至 N6 标准系列溶液中 Fe 基体浓度,均为每 mL 含 5 mg 铁。具体配制步骤参见附录 C2 及附录 C3。

表 2 标准系列溶液(N0~N6)

mg/L

元素 系列	Al	As	Co	Cr	Cu	Mn	Mo	Ni	P	Si	Sn	Ti	V	Fe
N0	0	0	0	0	0	0	0	0	0	0	0	0	0	5 000
N1	0.5	0.25	0.1	0.5	0.5	0.5	0.5	0.5	0.05	0.3	0.05	0.5	0.25	5 000
N2	1	0.5	0.2	1	1	1	1	1	0.1	0.6	0.1	1	0.5	5 000
N3	2	1	0.4	2	2	2	2	2	0.2	1.2	0.2	2	1	5 000
N4	10	5	2	10	10	10	10	10	15	6	1	10	5	5 000
N5	50	25	10	50	50	50	50	50	—	30	5	50	25	5 000
N6	—	—	—	100	—	100	—	—	—	60	—	—	—	5 000

5 仪器

采用电感耦合等离子体发射光谱仪。氩气纯度应 > 99.9%,以提供稳定清澈的等离子体炬焰。在仪器最佳工作条件下,进行测定。符合以下要求者,可以应用于本方法的测定。

5.1 仪器的稳定性

5.1.1 仪器短程稳定性

在点燃等离子 30 min 后,进行仪器的标准化,将质量浓度约为 10 mg/L 的各代表元素的溶液导入等离子体炬焰中,每次曝光 10 s,连续测量 10 次,此组数据不得任意取舍或补测。用 10 次连续测量值的相对标准偏差(RSD)表示仪器短程稳定性。规定 $RSD \leq 2.0\%$ (见 JJG 015—1996)。

5.1.2 仪器长程稳定性的检定

在点燃等离子体 30 min 后,进行仪器的标准化,将质量浓度约为 10 mg/L 的各代表元素的溶液导入等离子体炬焰中,每间隔 6 min 测量一次,每次曝光 10 s,共计测量 10 次,此组数据不得任意取舍或补测。用 10 次间隔测量值的相对标准偏差(RSD)表示仪器长程稳定性。规定 $RSD \leq 4.0\%$ (见 JJG 015—1996)。

5.2 仪器的检出限

制备两种溶液:空白溶液和 10 倍检出限单元素溶液。在这些溶液中含有与样品溶液相近的 Fe 基体,酸等试剂。空白溶液可用标准系列溶液 NO(4.8.3)。

在与被测试样溶液相同的条件下,喷入空白溶液(5.2)约 10 s。读取 10 次强度测定数值;在同一条件下,喷入 10 倍检出限的溶液(5.2)约 10 秒中,读取 10 次强度测定数值。

从所得强度数据,计算平均值 \bar{X}_i 和 \bar{X}_b 及标准偏差 S 。计算应保留四位有效数字。以下式计算 10 次测定的净强度平均值

$$\bar{X}_{ni} = \bar{X}_i - \bar{X}_b$$

式中: \bar{X}_{ni} ——净光强的平均值;

\bar{X}_i ——光谱强度平均值;

\bar{X}_b ——背景光谱强度平均值。

按下式计算所测元素的检出限:

$$DL = 3S \cdot C / \bar{X}_{ni}$$

这里, C 是 10 倍检出限溶液的浓度,为 mg/L。

本标准测定十三种元素仪器的检出限见附录 A。

5.3 校准(工作)曲线:回归曲线的线性相关系数应 $Y \geq 0.999$ 。

5.4 仪器工作条件参考附录 B。

6 分析步骤

6.1 试样质量 称取处理好的试样 0.500 0 克。

6.2 试样份数 称取两份试样进行测定,取其平均值。

6.3 空白试验 随同试样做空白试验。

6.4 测定

6.4.1 试样的处理

将试样(6.1)置于 100 mL 烧杯中,加入 30 mL 硝酸(4.6),3 mL 盐酸(4.2),放置片刻,待剧烈反应减缓后,加热溶解。当冒大气泡时,表明试样溶解充分,冷却后,移入 100 mL 容量瓶中,用水稀释至刻度,混均,待测。试样溶液如有碳化物沉淀,须沉静后测定清液。

6.4.2 校准曲线的制作

按顺序测定标准系列溶液 NO ~ N6(4.8.3)光谱强度,用计算机或计算器以净光强度为因变量,以元素的浓度($\mu\text{g/mL}$)为自变量进行线性回归,绘制工作曲线。计算出截距(a),斜率(b),和线性相关系数(r)。

6.4.3 谱线强度的测定

按实验要求及仪器规定,设置选定相应型号仪器的最佳分析条件,并调节仪器至最佳工作状态,测定空白溶液和试样溶液(6.4.1)中各待测元素的光谱强度,从工作曲线上计算出各相应组分的浓度。

7 分析结果的表述

按下式计算元素的百分含量:

$$W = \frac{(C_L - C_0) \times V}{m \times 10^6} \times 100$$

式中: W ——被测元素的含量, %;

C_0 ——从标准曲线查得的随同试样空白溶液中被测元素的浓度, $\mu\text{g/mL}$;

C_L ——从标准曲线查得的试样溶液中被测元素的浓度, $\mu\text{g/mL}$;

V ——被测试样溶液的体积, mL;

m ——试样质量, g。

8 精密度

精密度试验原始数据经 Grubbs 法检验、Cochran 法检验、Dixon 法检验, 剔除异常值后计算, 本精密度数据是在 1996 年由 10 个实验室对 7 个水平的试样所作的试验中确定的(见表 3)其中 Mn 的计算过程中 S_L^2 为负值。根据 GB/T 6379—1986 的规定, 令 $S_L^2 = 0$, 则 r 与 R 相一致。

表 3 精密度

元素	水平范围, % (m/m)	重复性, r	再现性, R
Al	0.013 ~ 0.180	$r = 0.0045 + 0.0183M$	$R = 0.0082 + 0.1513M$
As	0.012 ~ 0.109	$r = 0.0037 + 0.0552M$	$R = 0.0194 - 0.0302M$
Co	0.004 ~ 0.013	$r = 0.0004 + 0.1281M$	$R = 0.0042 + 0.0872M$
Cr	0.005 ~ 1.172	$r = 0.0027 + 0.0935M$	$R = 0.0089 - 0.1903M$
Cu	0.035 ~ 0.420	$r = 0.0707M^{0.8458}$	$R = 0.0040 + 0.0862M$
P	0.011 ~ 0.055	$r = 0.0028 + 0.0247M$	$R = 0.0034 + 1.2523M$
Mn	0.310 ~ 1.531	$r = 0.0742 + 0.0172M$	$R = 0.0742 + 0.0172M$
Mo	0.008 ~ 0.633	$r = 0.0022 + 0.0936M$	$R = 0.0081 + 0.1779M$
Ni	0.014 ~ 0.138	$r = 0.0042 + 0.1106M$	$R = 0.0563M^{0.3954}$
Si	0.065 ~ 0.805	$r = -0.0002 + 0.1258M$	$R = 0.0011 + 0.3144M$
Sn	0.003 ~ 0.036	$r = 0.0038 + 0.0597M$	$R = 0.0062 + 0.0105M$
Ti	0.004 ~ 0.658	$r = -0.0006 + 0.2313M$	$R = 0.0050 + 0.2779M$
V	0.001 ~ 0.322	$r = 0.0005 + 0.1026M$	$R = 0.0012 + 0.2785M$

本方法在正常情况下, 由同一操作人员, 在同一实验室内, 使用同一仪器, 并在短期内, 对同一试样所作两个单次测定结果之间的差值超过重复性 r 平均来说 20 次中不多于 1 次。

本方法在正常操作情况下, 由两名操作人员, 在不同实验室, 对同一试样所作两个单次测定结果之间的差值超过再现性 R 平均来说 20 次中不多于 1 次。

如果两个独立测试结果之间的差值, 超过了表 3 中所列精密度函数关系式算出的重复性或再现性数值, 则认为这两个结果是可疑的。

9 安全注意事项

9.1 应按高压钢瓶安全操作规定使用高压氩气钢瓶。

9.2 仪器室排风良好, 等离子体炬焰中产生的废气或有毒蒸气应及时排除。

9.3 点燃等离子体后, 应尽量少开蔽门, 以防高频辐射伤害身体。

9.4 注意安全用电。

附录 A

(提示的附录)

不同仪器测定十三种元素(铁基)的检出限

表 A1 不同仪器测定十三种元素(铁基)的检出限

 $\mu\text{g/mL}$

仪器型号	Al	As	Co	Cr	Cu	P	Mn
ICPV-1014(京)	0.013	0.058	0.006	0.015	0.010	0.071	0.009
BAIRD PS4(闽)	0.035	0.023	0.004	0.005	0.007	0.051	0.002 0
JY-70P(津)	0.037	0.038	0.044	0.021	0.008	—	0.088
JY-70P(赣)	0.062	—	0.042	0.006 7	0.004 7	—	0.013
仪器型号	Mo	Ni	Si	Sn	Ti	V	
ICPV-1014(京)	0.015	0.017	0.065	0.043	0.011	0.007	
BAIRD PS4(闽)	0.011	0.006	0.028	0.012	0.006	0.006	
JY-70P(津)	0.059	0.035	0.062	—	0.008	0.026	
JY-70P(赣)	0.070	0.031	0.015	—	0.002	0.001 3	

附录 B

(提示的附录)

不同型号 ICP—AES 光谱仪的工作条件(参考)

表 B1 使用五种型号 ICP—AES 光谱仪的工作条件(参考)

光谱仪型号	岛津 ICPV-1014	BAIRD PS-4	JY-70P	Labtam8440-MS	ARL3520-AES
道数	多道(n+1)	多道	单道(多道)	单道(n+m)	单道
焦距, M	1	1	1	0.75/1	1
光栅刻线, 条/mm	1 920 2 160	1 440 1 800	3 600	1 400 1 800	1 080
波长范围, nm	175.0~460.0 165.0~413.7	173.0~767.0 170.0~800.0	— —	170~800	165~800
线色散率倒数, nm/mm	0.52(1 920) 0.46(2 160)	0.66(1 440) 1.1(1 800)	—	0.75	0.023
入射功率, kW	1.2	1.25	1.8	1.2	1.2
高频功率发生器 反射功率, W	<5	<3	<3	<5	—
工作频率, MHz	27.12	27.12	40.68	—	—
观察高度, mm	15	12	14	10	—
冷却气, L/min	12	9.5	14	13	12
辅助气, L/min	0.9	0.55	0.4	1.23	0.8
气路系统 载气, L/min	0.7	0.65	0.4	0.98	0.35
净化气, L/min	3.0	2.0	—	—	—
氩气纯度, %	99.95	99.95	99.95	—	—
氩气分压, Pa	4.4×10	5.0×10	—	—	—
炬管	三层同心 石炬管	低气流炬管	可拆式 同炬管	可拆式	—
雾化装置	气动式	WU-喷雾器 旋流雾室	气动式	GMK 雾化器	三管同心 玻璃雾化器

表 B1(完)

光谱仪型号	岛津 ICPV-1014	BAIRD PS-4	JY-70P	Labtam8440-MS	ARL3520-AES
样品提取量, mL/min	1.8	2	4	3	1.8
数据处理系统	型号 QC6	IBM 286	APPLEII 182	IBM 386	DPS/II/2364
	积分时间, s 20	5	3	10	5
	积分次数 3	4	3	3	—
单 位	商检研究所 上海商检局 辽宁商检局	厦门商检局	天津商检局 江西商检局	广东商检局	广西商检局

表 B2 分析谱线波长

元素	Al	As	Co	Cr	Cu	Mn	Mo	Ni	P	Si	Sn	Ti	V	
波长	1	396.1	193.7	288.6	267.7	324.7	257.6	281.6	231.6	178.2	251.6	189.9	334.9	311.0
nm	2	308.2	197.2	345.3	—	—	—	202.0	—	213.6	288.1	242.9	337.2	310.2
	3	—	189.0	228.6	—	—	—	—	—	—	—	—	—	292.4

附 录 C

(提示的附录)

标准溶液的配制

表 C1 多元素标准溶液(2倍 N5)的配制

元 素	单元素标液浓度 $\mu\text{g/mL}$	总量 $2\text{N5} \times 200 \text{ mL}$ μg	应取单元素标液体积 mL	备 注
Al	1 000	20 000	20	按本表所列数值吸取单元素质标液 200 mL 容量瓶中,用水稀至刻度
As	1 000	10 000	10	
Co	1 000	4 000	4	
Cr	1 000	20 000	20	
Cu	1 000	20 000	20	
P	1 000	2 000	2	
Mn	1 000	20 000	20	
Mo	1 000	20 000	20	
Ni	1 000	20 000	20	
Si	500	12 000	24	
Sn	500	2 000	4	
Ti	1 000	20 000	20	
V	1 000	10 000	10	

表 C2 标准系列 N0 ~ N5(铁基 5)溶液的配制(Al 为例)

系列	浓度 $\mu\text{g}/\text{mL}$	量 $\mu\text{g}(100\text{ mL})$	应取 2N5 的体积 mL	应取 N4($10\ \mu\text{g}/\text{mL}$) 的体积 mL	应取 Fe 溶液(5 mL) 的体积, mL	备 注
2N5	100	—	—	—	—	按计算数数值吸取 2 倍 N5 混合标液和铁基体溶液于 100 容量瓶中用盐酸(1 + 11)稀至刻度
N5	50	5 000	50	—	10	
N4	10	1 000	10	—	10	
N3	2	200	2	—	10	
N2	1	100	—	10	9.75	
N1	0.5	50	—	5	9	
N0	—	—	—	—	10	

表 C3 混合标准系列 N6(Cr、Mn、Si)的配制(总体积 100 mL)

元 素	浓度 $\mu\text{g}/\text{mL}$	总量, μg (100 mL)	单质标液浓度 $\mu\text{g}/\text{mL}$	应取体积 mL	备 注
Cr	100	10 000	1 000	10	按本表所列计算数值吸取单质标液和铁基体溶液 10 mL 于 100 mL 容量瓶中用盐酸(1 + 11)稀至刻度
Mn	100	10 000	1 000	10	
Si	60	6 000	500	12	

Foreword

This standard was drafted in accordance with the requirements of GB/T 1.1—1993 “Directives for the work of standardization Unit 1: Drafting and presentation of standards Part 1: General rules for drafting standards”. The drafting of this standard is abided by the stipulations of GB/T 1.2—1996、GB/T 1.4—1988、GB/T 1467—1978, and GB/T 10725—1989.

The determination limits in this standard are defined according to the different element content of carbon steel and low alloyed steel for different brand.

The standard has been proposed by the charge for the State Administration of Import and Export Commodity Inspection of the People's Republic of China.

The main drafting unit was as follows: the China Import and Export Commodity Inspection Technology Institute.

The units participated in the developing of this standard were as follows: China Import and Export commodity Inspection Technology Institute, Xia Men Import and Export commodity Inspection Bureau, Tian Jin Import and Export commodity Inspection Bureau, Guang Dong Import and Export commodity Inspection Bureau, Guang Xi Import and Export commodity Inspection Bureau, Liao Ning Import and Export commodity Inspection Bureau, Hu Nan Import and Export commodity Inspection Bureau, Shang Hai Import and Export commodity Inspection Bureau, Jiang Su Import and Export commodity Inspection Bureau, Jiang Xi Import and Export commodity Inspection Bureau,

This standard was mainly drafted by Meng Lanxing, Zhao Guohua, He Boling, wang Honghui, Liu Shenglin, Wang Jinling, Zhao Henying.

Professional Standard of the People's Republic of China
for Entry-Exit Inspection and Quarantine

**Import and export carbon steel and low
alloyed steel—Determination of
aluminium, arsenic, chromium, cobalt,
copper, phosphorus, manganese, molybdenum,
nickel, silicon, tin, titanium, and vanadium
content—Inductively coupled plasma
atomic emission spectrometric method**

SN/T 0750—1999

1 Scope

This standard specifies the inductively coupled plasma atomic emission spectrometric method (abbreviated as ICP—AES) of determination of aluminium, arsenic, cobalt, chromium, copper, phosphorus, manganese, molybdenum, nickel, silicon, tin, titanium, and vanadium thirteen elements' content of carbon steel and low alloyed steel, and its limits of determination are indicated in Table 1.

Table 1 Limits of determination of thirteen elements % (m/m)

Element Det. limits	Al(s)* 0.01 ~ 0.50	As 0.005 ~ 0.10	Co 0.005 ~ 0.01	Cr 0.01 ~ 1.0	Cu 0.01 ~ 0.5
Element Det. limits	P 0.01 ~ 0.05	Mn 0.01 ~ 1.5	Mo 0.01 ~ 0.5	Ni 0.01 ~ 0.1	Si 0.05 ~ 0.5
Element Det. limits	Sn 0.005 ~ 0.1	Ti 0.01 ~ 0.50	V 0.005 ~ 0.5		

* (s) means acid-soluble aluminium.

2 Normative references

The clauses included in the following standards have been quoted in this standard, and they constituted articles of this standard. The editions indicated were valid, when the standard was published. The all standards could be revised. Each side using this standard has to approach a possi-

bility of using the latest edition of following standards.

GB/T 6682—1992 The specifications using water in the laboratories and test method

GB 10725—1989 Chemical reagent The general rules of inductively coupled plasma atomic emission spectrometric method

JJG 015—1996 The appraisal rules of inductively coupled plasma atomic emission spectrograph

GB/T 6379—1986 The determination of method precision The determination of repeatability and reproducibility of standard test method by means of test among the laboratories

3 Summary

After dissolving the sample in the mixture of hydrochloric and nitric acids and diluting to determined volume, its solution is nebulized into flame of inductively coupled plasma used as an excitation source for emission spectrograph. At the wavelength of corresponding element in the inductively coupled plasma atomic emission spectrograph, and its spectral intensity is measured.

4 Reagents and solutions

In this experiment the analytically pure reagents and de-ionized water accorded with the stipulations of GB/T 6682 were used only except special note.

4.1 High purity iron (the iron content > 99.98%)

4.2 Hydrochloric acid

4.3 Nitric acid

4.4 Hydrochloric acid (1 + 1)

4.5 Hydrochloric acid (1 + 11)

4.6 Nitric acid (1 + 5)

4.7 Iron matrix solution: Weigh 5.000 0 g of high purity iron (4.1), put it in a beaker of 250 mL. Add 40 mL of hydrochloric acid (4.4) in the beaker, then cover it with watch glass and slightly heat it till iron is completely solved, cool it at the room temperature. Wash the watch glass with a small amount of water. Transfer the solution into a measuring flask of 100 mL and dilute it with de-ionized water until the graduation, mix it homogeneously for reserve. The concentration of this so-

lution of iron is 50 mg/mL.

4.8 Standard solution

4.8.1 Single element standard solution for 13 elements: Every single element standard solution can be purchased from selling standard substance unit approved by the State. Its mass concentration is 1 000 mg/mL (or 500 mg/mL).

4.8.2 Multielement standard solution (two times N5): the solution is prepared with the single element standard solution (4.8.1) according to Table 2., namely, separately calculate the single element standard solution volume corresponded to two times N5. Separately take the single element standard solution for 13 elements (4.8.1) according to the calculated volume and put it in measuring flask of 200 mL, dilute it to 200 mL with hydrochloric acid (4.5), prepare multielement standard solution (two times N5) for reserve. In the process of preparation, the concentration of hydrochloric acid should be kept in about 1 mol/L preventing the tin hydrolysis and the silicon separating out.

4.8.3 Series standard solutions (N0 ~ N6): separately take 10 mL of iron matrix solution and put in seven measuring flasks. Calculate the volumes according to Table 2. Separately take two times calculated volume of N5 (4.8.2) multielement standard solution and put it in three measuring flasks of seven flasks, dilute it with hydrochloric acid (4.5) until graduation, prepare series standard solutions from N3 to N5. Then separately take calculated volume of N4 standard solution and put it in another two measuring flasks, dilute it with hydrochloric acid (4.5) until graduation and prepare N1 and N2. Separately take 10 mL of chromium and manganese single element standard solution and 12 mL of silicon, put it in the sixth measuring flask and dilute it with hydrochloric acid (4.5) until graduation, prepare N6 of series standard solution. The seventh flask solution is N0. The every iron matrix concentration of series standard solutions from N0 to N6 is 5 mg/mL. The practical procedure of preparation can be seen in annex C.

Table 2 Series mixture standard solutions (N0 ~ N6) mg/L

Element	Al	As	Co	Cr	Cu	Mn	Mo	Ni	P	Si	Sn	Ti	V	Fe
N0	0	0	0	0	0	0	0	0	0	0	0	0	0	5 000
N1	0.5	0.25	0.1	0.5	0.5	0.5	0.5	0.5	0.05	0.3	0.05	0.5	0.25	5 000
N2	1	0.5	0.2	1	1	1	1	1	0.1	0.6	0.1	1	0.5	5 000
N3	2	1	0.4	2	2	2	2	2	0.2	1.2	0.2	2	1	5 000
N4	10	5	2	10	10	10	10	10	15	6	1	10	5	5 000
N5	50	25	10	50	50	50	50	50	—	30	5	50	25	5 000
N6	—	—	—	100	—	100	—	—	—	60	—	—	—	5 000

5 Apparatus

The inductively coupled plasma atomic emission spectrograph is used. The argon gas used in

this experiment has to be pure enough (> 99.9%) for getting a stable and clear plasma torch flame. The determination can be done on the best working condition of the apparatus. This method can be used for determination, according with the requirements as following.

5.1 Stability of instrument

5.1.1 Short-term stability

The apparatus has been standardizing after 30 min, when the plasma was lighted. The every representative element solution with mass concentration of 10 mg/L was introduced into plasma torch flame. It was exposed once 10 s and continuously determined ten times. The wanton acceptance and rejection or additional determination of this group of data were not allowed. The short-term stability of the apparatus was expressed by the relative standard deviation (RSD) for ten times' continuous determination. It was provided that $RSD < 2.0\%$ or $RSD = 2.0\%$ (see JJG 015—1996).

5.1.2 Examination and determination of the long-term stability of the apparatus

The apparatus has been standardizing after 30 min, when the plasma was lighted. The every representative element solution with mass concentration of 10 mg/L was introduced into plasma torch flame. It was determined once at intervals of six minutes and exposed once 10 s. It was totally determined ten times. The wanton acceptance and rejection or additional determination of this group of data were not allowed. The long-term stability of the apparatus was expressed by the relative standard deviation (RSD) for ten times' discontinuous determination. It was provided that $RSD < 4.0\%$ or $RSD = 4.0\%$ (see JJG 015—1996).

5.2 Detection limit of instrument

Prepare two solutions: blank solution and ten times detection limit single element solution. The iron matrix, acid and other reagent content of these solutions and sample solution is similar. NO of the series standard solution (4.8.3) can be used as blank solution.

Spray blank solution (5.2) about 10 s on condition every experiment parameter is identical with that for determined sample solution. Take the data for ten times' intensity determination. On the same conditions, spray ten times detection limit single element solution (5.2) about 10 s, take the data for ten times' intensity determination. Calculate average values \bar{X}_i , \bar{X}_b , and standard deviation S . Calculation has to keep, four significant digits. Calculate average value of net intensity for ten times' determination by following formula.

$$\bar{X}_{ni} = \bar{X}_i - \bar{X}_b$$

In the formula, \bar{X}_{ni} —average value of net intensity;

\bar{X}_i —the mean of spectral intensity;

\bar{X}_b —the mean of background spectral intensity.

Calculate the detection limit of the determined element by following formula:

$$DL = 3S \cdot C / \bar{X}_{ni}$$

Here C is the concentration of ten times detection limit solution (mg/L).

The detection limit of the apparatus for 13 determined elements can be seen in annex A.

5.3 Correction (working) curve: linear correlation coefficient of regression curve (r) is 0.999.

5.4 Working conditions (see annex B)

6 Procedure of analysis

6.1 Sample mass weigh 0.5 g of treated sample with accuracy 0.000 1 g.

6.2 Sample portions weigh and determine duplicate samples, take its mean.

6.3 Blank test blank test was finished with the sample.

6.4 Determination

6.4.1 Sample treatment

Put the sample (6.1) into the 100 mL-beaker, add 30 mL of nitric acid (4.6) and 3 mL of hydrochloric acid (4.2). Wait a moment, when the sample is completely dissolved and cool, transfer the solution into the 100 mL-measuring flask, dilute it with water to 100 mL graduation, homogeneously mix it and reserve it for determination. If there is some carbonide sediment in the sample solution, use the clear liquor after complete precipitation.

6.4.2 The making of correction curve

Determine the spectral intensities of the series standard solutions N0 ~ N6 (4.8.3) in sequence. Draw the working curve using computer or calculator and conducting linear regression with net intensity as dependent variable and element concentration as independent variable. Calculate the linear correlation coefficient (r).

6.4.3 Determination of spectral intensity

Set up the best analytical conditions of the apparatus with selected type and adjust it to best working state in accordance with experiment requirements and instrument stipulations. Determine the spectral intensities of the determined elements in the blank and sample solutions (6.4.1). Calculate the concentrations of the corresponding content from the working curve.

7 Expression of results

Calculate the element content by following formula:

$$W = (C_i - C_o) \times V \times 100 / m \times 10^6$$

In the formula, W — element content determined, %;

C_o —concentration of the determined element in blank solution, getting from standard curve, mg/L;

C_i —concentration of the determined element in sample solution, getting from standard curve, mg/L;

V —volume of determined sample solution, mL;

m —sample mass, g.

8 Precision

The original data of precision have been examined by Grubbs method, Cochran method and Dixon method. The precision has been got by calculation after injecting abnormal value. The precision data were defined by ten laboratories' test with seven levels' samples for each determined element content in the year 1996 (see Table 3.), among them S1 was negative value in the process of the calculation for Mn. According to rules of GB/T 6379—1986, make $S_L^2 = 0$, so r is consistent with R .

Table 3 Precision

Element	Limits of determination % (m/m)	Repeatability r	Reproducibility R
Al	0.013 ~ 0.180	$r = 0.004\ 5 + 0.018\ 3M$	$R = 0.008\ 2 + 0.151\ 3M$
As	0.012 ~ 0.109	$r = 0.003\ 7 + 0.055\ 2M$	$R = 0.019\ 4 - 0.030\ 2M$
Co	0.004 ~ 0.013	$r = 0.000\ 4 + 0.128\ 1M$	$R = 0.004\ 2 + 0.087\ 2M$
Cr	0.005 ~ 1.172	$r = 0.002\ 7 + 0.093\ 5M$	$R = 0.008\ 9 - 0.190\ 3M$
Cu	0.035 ~ 0.420	$r = 0.070\ 7M^{0.845\ 8}$	$R = 0.004\ 0 + 0.086\ 2M$
P	0.011 ~ 0.055	$r = 0.002\ 8 + 0.024\ 7M$	$R = 0.003\ 4 + 1.252\ 3M$
Mn	0.310 ~ 1.531	$r = 0.074\ 2 + 0.017\ 2M$	$R = 0.074\ 2 + 0.0172M$
Mo	0.008 ~ 0.633	$r = 0.002\ 2 + 0.093\ 6M$	$R = 0.008\ 1 + 0.177\ 9M$
Ni	0.014 ~ 0.138	$r = 0.004\ 2 + 0.110\ 6M$	$R = 0.056\ 3M^{0.395\ 1}$
Si	0.065 ~ 0.805	$r = -0.000\ 2 + 0.125\ 8M$	$R = 0.001\ 1 + 0.314\ 4M$
Sn	0.003 ~ 0.036	$r = 0.003\ 8 + 0.059\ 7M$	$R = 0.006\ 2 + 0.010\ 5M$
Ti	0.004 ~ 0.658	$r = -0.000\ 6 + 0.231\ 3M$	$R = 0.005\ 0 + 0.277\ 9M$
V	0.001 ~ 0.322	$r = 0.000\ 5 + 0.102\ 6M$	$R = 0.001\ 2 + 0.278\ 5M$

In normal case, the difference between two single determination results exceeded the repeatability r no more than once among 20 times according to the average, using this method with same instrument and same sample in same laboratory by same operator in the short run.

In normal case of operation, the difference between two single determination results exceeded the reproducibility R no more than once among 20 times according to the average, using same sample in different laboratories by two operators.

If the difference between two independent determination results exceeded repeatability or reproducibility calculated by precision function relationship indicated in Table 3, the two results were suspicious.

9 The safety points for attention

- 9.1 Use high-pressure argon bottle in accordance with the safety operation rules of high-pressure bottle.
- 9.2 There is good exhaust in the instrument room, and the waste or noxious gas produced from the plasma torch flame should be promptly removed.
- 9.3 Open and shut the door as little as possible after lighting the plasma for preventing harm the health from high-frequency radiation.
- 9.4 Pay attention to safety use of electricity.

宁波市镇海区质量技术监督检测中心

Annex A

(informative)

Detection limits of thirteen elements (on iron base) with different instruments

Table A1 Detection limits for thirteen elements with different instruments, $\mu\text{g/mL}$

Element	Al	As	Co	Cr	Cu	P	Mn
ICPV-1014	0.013	0.058	0.006	0.015	0.010	0.071	0.009
BAIRD PS4	0.035	0.023	0.004	0.005	0.007	0.051	0.002 0
JY-70P(Tian Jin)	0.037	0.038	0.044	0.021	0.008	—	0.088
JY-70P(Jiang Xi)	0.062	—	0.042	0.006 7	0.004 7	—	0.013
Element	Mo	Ni	Si	Sn	Ti	V	
ICPV-1014	0.015	0.017	0.065	0.043	0.011	0.007	
BAIRD PS4	0.011	0.006	0.028	0.012	0.006	0.006	
JY-70P(Tian Jin)	0.059	0.035	0.062	—	0.008	0.026	
JY-70P(Jiang Xi)	0.070	0.031	0.015	—	0.002	0.001 3	

Annex B

(informative)

Working conditions for different type ICP—AES s(reference)

Table B1 working conditions with five type ICP—AES

Type of spectrometer	ICPV-1014	BAIRD PS-4	JY-70P	Labtam8440 MS	ARL3520 -AES
Channel number	Multich. (n + 1)	Multich.	Single & Multich.	Single (n + m)	Single
Focal distance, m	1	1	1	0.75/1	1
Grating lines, gr./mm	1 920 2 160	1 440 1 800	3 600	1 400 1 800	1 080
Wavelength range, nm	175.0 ~ 460.0 165.0 ~ 413.7	173.0 ~ 767.0 170.0 ~ 800.0	— —	170 ~ 800	165 ~ 800
Reciprocal linear Dispersion, nm/mm	0.52(1 920) 0.46(2 160)	0.66(1 440) 1.1(1 800)	—	0.75	0.023
High freq. Incident Power gen power, kW	1.2	1.25	1.8	1.2	1.2
Reflection Power, W	<5	<3	<3	<5	—
Working Frequency, MHz	27.12	27.12	40.68	—	—
Observed altitude, mm	15	12	14	10	—
Gas-system					

Table B1(concluded)

Type of spectrometer	ICPV-1014	BAIRD PS-4	JY-70P	Labtam8440 MS	ARL3520 -AES	
Cooling gas, L/min	12	9.5	14	13	12	
Supp. gas, L/min	0.9	0.55	0.4	1.23	0.8	
Carr. gas, L/min	0.7	0.65	0.4	0.98	0.35	
Cleansing. gas, L/min	3.0	2.0	—	—	—	
Argon pur, %	99.95	99.95	99.95	—	—	
Argon par. Tial pres. , Pa	4.4×10^5	5.0×10^5	—	—	—	
Torch	Triple quartz tor. (concentric)	Low gas Flow torch	Disass. Torch	Disassem. Concentric Torch	—	
Nebulization device	pneumatic	WU- nebulizer Whirl chamber	Pneumatic	GMK-nebul.	Triple glass Concentric	
Sampling size(mL/min)	1.8	2	4	3	1.8	
Data-pro- Cessing- System	Type Integral (sec) Integral Frequence	QC6 20 3	IBM 286 5 4	APPLEII 182 3 3	IBM 386 10 3	DPS/II/2364 5 —
Unit	CIE CITI SH CIB LN CIB	XM CIB	TJ CIB JX CIB	GD CIB	GX CIB	

Table B2 Spectral line wavelength for analysis

Element	Al	As	Co	Cr	Cu	Mn	
Wave length nm	1 396.1	193.7	288.6	267.7	324.7	257.6	
	2 308.2	197.2	345.3	—	—	—	
	3 —	189.0	228.6	—	—	—	
Element	Mo	Ni	P	Si	Sn	Ti	V
Wave length nm	1 281.6	231.6	178.2	251.6	189.9	334.9	311.0
	2 202.0	—	213.6	288.1	242.9	337.2	310.2
	3 —	—	—	—	—	—	292.4

Annex C

(informative)

Preparation of standard solutions

Table C1 Preparation of multielement standard solutions (two time N5)

Element	Concentration of Simple subs. stan. $\mu\text{g/mL}$	Total content (2N5 \times 200 mL) μg	Simple subs. Stand. solution mL	Remarks
Al	1 000	20 000	20	For prepa-multi- element st. solu- tion water is used as di-Luent.
As	1 000	10 000	10	
Co	1 000	4 000	4	
Cr	1 000	20 000	20	
Cu	1 000	20 000	20	
P	1 000	2 000	2	
Mn	1 000	20 000	20	
Mo	1 000	20 000	20	
Ni	1 000	20 000	20	
Si	500	12 000	24	
Sn	500	2 000	4	
Ti	1 000	20 000	20	
V	1 000	10 000	10	

Table C2 Preparation of series standard solution with iron matrix (5 mg/mL)

Series	Concent. $\mu\text{g/mL}$	Total Content μg	2N5-volume mL	N4-volume mL	Fe-matrix (50 mg/mL)	Remarks
2N5	100	—	—	—	—	Hydrochloric acid (1 + 11) is used as diluent to 100 mL
N5	50	5 000	50	—	10	
N4	10	1 000	10	—	10	
N3	2	200	2	—	10	
N2	1	100	—	10	9.75	
N1	0.5	50	—	5	9	
N0	—	—	—	—	10	

Table C3 Preparation of N6-mixture standard solution

Element	Concentr. $\mu\text{g/mL}$	Total cont. μg	Simple subs. Stand. solut. Conc. $\mu\text{g/mL}$	Volume mL	Remarks
Cr	100	10 000	1 000	10	Hydrochloric acid (1 + 11) is used as diluent
Mn	100	10 000	1 000	10	
Si	60	6 000	500	12	

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