Analysis of Metal Alloys by Inductively Coupled Argon Plasma Optical Emission Spectrometry

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A technique for analyzing metal alloys using a direct-reading inductively coupled argon plasma (ICAP) spectrometer is described in which samples are acid-dissolved before analysis. Because a concentration ratio method is used for analysis, dilution errors of up to ±40% can be tolerated without significant loss of accuracy. The ICAP technique is used to determine 17 elements in irons and steels, 14 elements in copper-based alloys, and 12 elements in aluminum alloys. The analytical accuracy of these determinations is verified by the analysis of standard reference materials for each sample matrix.

Routine analyses of metal alloys in quality control laboratories are performed most commonly by spark emission spectrometry or X-ray fluorescence because of rapid sample turnaround and ease of operation. The problem with both of these techniques is that the analytical signal is highly dependent on matrix composition. Precise matching of sample and standard matrices is required if accurate results are to be obtained. However, certified standards for calibration that match the samples to be analyzed often are difficult to find. Other alternatives, e.g., wet chemistry procedures, are unaffected by the certified standards problem because synthetic standards can be prepared readily, but such methods are time-consuming. Also, analytical determinations must be made sequentially, compounding the time factor. Atomic absorption spectrometry is a faster analytical technique than wet chemistry but, again, determinations are made sequentially. The inductively coupled argon plasma (ICAP) spectrometry technique has positive characteristics for application to metal alloy analysis, i.e., its simultaneous, multielement determination capability and its use of synthetic standards.

Fassel and Dickinson (*1*) described a method of analyzing arsenic and tin in solders that involved melting the sample, forming an aerosol by ultrasonic nebulization, and analyzing the aerosol by ICAP. Hoare and Mostyn (*2*) described a high frequency plasma method for determining boron and zirconium in nickel-based alloys following sample dissolution. Souilliart and Robin (*3*) described a method for determining hafnium in zirconium by ICAP. Kirkbright and Ward (*4*) compared the ICAP with flame emission using a separated nitrous oxide–acetylene flame for the determination of copper, zinc, iron, titanium, manganese, and magnesium in aluminum alloys and concluded that the ICAP gave better precision and offered simultaneous multichannel analytical capability.

Butler et al. (*5*) described a procedure for the determination of aluminum, chromium, copper, manganese, and nickel in steel samples using an ICAP spectrometer that had been calibrated with synthetic standards prepared in the presence of iron only. With this minimal matrix matching, these workers were able to analyze low alloy, high alloy, and stainless steels with the same calibration curve.

Other applications of the ICAP to metal alloy analyses in which several elements have been determined in various sample matrices also have been reported in the literature (*6–10*). However, none of these reports has covered the simultaneous multielement analysis of the metal alloy sample in a truly comprehensive fashion.

In this paper, we describe the analysis of iron-based, copper-based, and aluminum-based alloys in which the majority of the alloying components is determined and the concentration ratio method of analysis employed. The concentration ratio method offers a potential analytical advantage; only relative solution concentrations rather than absolute solution concentrations are required for analysis. Consequently, there is no need to weigh the initial sample or measure the final volume accurately, provided that the solution concentrations of both analyte and matrix are within the instrument's calibration range. The elimination of the need for accurate sample weighing not only speeds up sample preparation but also prevents any potential errors that may be caused by misreading or mistakes in arithmetic or transcription.

EXPERIMENTAL

Theory. Because the concentration ratio method of analysis is described fully elsewhere (*11*), only a brief discussion will be presented here.

If the concentration of the ith analyzed element in the original sample is C_i, the concentration of the jth unanalyzed element is C_j and the matrix element concentration is C_M, then

$$\sum_i C_i + \sum_j C_j + C_M = 100 \tag{1}$$

where all concentrations are in percentages. This equation then may be arranged to the form:

$$1 + \frac{\sum C_i}{C_M} = 1 + \sum_i B_i = \frac{100 - \sum_j C_j}{C_M} \tag{2}$$

where B_i is the concentration ratio of the ith element to the matrix element.

When the analytical technique exhibits a linear relationship between signal and concentration, then the ratio of the net line intensity of the ith element to the matrix element, R_i, may be described by Equation 3, where p_i and q_i are calibration constants:

$$R_i = p_i + q_i B_i \tag{3}$$

Given this, the concentration ratio technique should give equivalent data regardless of the absolute solution concentrations and hence be independent of the weight of solid used or the final dilution volume.

Once the concentration ratios and any residual concentration (C_j) have been determined, then Equation 2 may be solved to determine the matrix element concentration (C_M). From this value and the determined concentration ratio (B_i), the absolute concentration of the ith element in the original sample is calculated from Equation 4:

$$C_i = B_i C_M \tag{4}$$

If the relationship is not linear, however, this freedom from solution concentration and the concentration ratio technique are not valid. For example, if the analytical equation is second order, Equation 3 is modified to Equation 5, where p_i, q_i, and r_i are the

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Table I. Elements and Analytical Wavelengths (nm) Employed

element	copper line	copper bkgd[a]	iron line	iron bkgd[a]	aluminum line	aluminum bkgd[a]
Ag	328.068	328.102	...[b]	...	...[b]	...
Al	308.215	308.249	308.215	308.249	308.215[c]	...
As	193.696	193.730	193.696	193.730	...[b]	...
B	...[b]	...	249.773	249.807	...[b]	...
Cd	226.502	226.536	...[b]	...	...[b]	...
Co	...[b]	...	228.616	228.650	...[b]	...
Cr	...[b]	...	267.716	267.750	267.716	267.750
Cu	213.598[c,d]	...	324.754	324.788	324.754	324.788
Fe	259.940	259.974	238.863[c]	...	259.940	259.974
Mg	...[b]	...	...[b]	...	383.231[d]	...
Mn	257.610	257.644	257.610	257.644	257.610	257.644
Mo	...[b]	...	202.030	202.064	...[b]	...
Nb	...[b]	...	313.079	313.113	...[b]	...
Ni	231.604	231.621	231.604	231.621	231.604	231.621
P	253.565	253.599	214.914	214.931	...[b]	...
Pb	220.353	220.387	...[b]	...	220.353	220.387
Sb	217.581	217.615	...[b]	...	217.581	217.615
Si	288.158	288.192	288.158	288.192	...[b]	...
Sn	189.989	190.023	...[b]	...	189.989	190.023
Ta	...[b]	...	240.063[d]	...	...[b]	...
Ti	...[b]	...	334.941	334.978	334.941	334.978
V	...[b]	...	292.402	292.436	...[b]	...
W	...[b]	...	207.911	207.945	...[b]	...
Zn	206.200	206.217	...[b]	...	213.856	213.890
Zr	...[b]	...	339.198	339.222	...[b]	...

[a] Background measurement wavelength. [b] Signifies element not determined. [c] Signifies used as internal standard, no background correction employed. [d] Line selected on external monochromator.

Table II. Operating Conditions

ICAP	
Plasma torch	Quartz type, 1-mm nozzle diameter
Argon gas flows	Coolant—18 L/min Auxiliary—0.5 L/min Sample—0.7 L/min
Peristaltic pump	Gilson Minipuls II
Solution uptake rate (pumped)	0.95 mL/min
Forward RF power	1.2 kW
Reverse RF power	<5 W
Induction coil	Three-turn water-cooled copper tubing
Optics	
Focusing element	Separate off-axis front-surfaced concave mirrors for direct reader and monochromator
Magnification	×3.6 nominal
Height of observation plasma	18 mm above coil
Entrance slit aperture	3 mm
Direct reader	
Entrance slit	25 μm
Exit slits	50 μm
Grating	2360 gr/mm ruled concave
Blaze	270 nm
Direct reader	
Dispersion	0.53 nm/mm first order
Monochromator	
Entrance slit	10 μm
Exit slit	20 μm
Grating	1180 gr/mm ruled plain
Blaze	270 nm
Dispersion	1.6 nm/mm first order
Electronics	
PMT	Hamamatsu type R427—185-200 nm direct reader, R300—250-500 nm direct reader, R456—185-800 nm monochromator
Voltage	600-950 V
Read out	Central processing unit (PDP-8A, DEC, Maynard, Mass.), controlled individual op-amp analog integrators with multiplexed A/D converters
Integration period	14 s—line 7 s—background
CPU terminal	LA-36 DECwriter (DEC, Maynard, Mass.)
CPU mass storage	RX01 Dual Floppy Disks (DEC, Maynard, Mass.)

calibration constants and C'_i is the solution concentration of the ith element:

$$R_i = p_i + q_iB_i + r_iB_iC'_i \qquad (5)$$

Since Equation 5 has two unknowns, B_i and C'_i, it is impossible to use the concentration ratio method from a single measurement. Reasonable approximations can be made if either, or preferably both, the terms r_i and C'_i are small, and the matrix element constitutes over 90% of the sample and remains fairly constant. If the matrix element is subject to large variations in concentration and constitutes only 50–70% of the sample, e.g., iron in stainless or high alloy steels, or copper in brass, then the likelihood for substantial error exists, especially for the major alloying elements.

Spectral Line Interference Corrections. In any emission spectroscopic technique, the possibility always exists of spectral line interferences from a concomitant species upon the analyte line. The ICAP technique is no exception to this condition. The high precision of the ICAP coupled with the ease with which synthetic standards can be prepared makes the correction of spectral interferences a much simpler task when compared with other emission techniques.

In the spectrometer data processing unit, corrections for spectral line overlap are made on the ith element from the kth element using Equation 6, where B_i is the corrected concentration ratio,

Table III. Linear Calibration Verification Standards

Copper

% w_a/w_m[a] in sample	mg/L in solution	elements
0, 0.05, 0.1, 0.2	0, 2.5, 5, 10	Ag, As, Cd, Mn, Ni, P, Sb, Si
0, 0.2, 0.5, 1.0, 2.0	0, 10, 25, 50, 100	Fe, Sn
0, 0.5, 1.0, 2.0, 5.0	0, 25, 50, 100, 250	Al, Pb
0, 1, 5, 10, 20, 50	0, 50, 250, 500, 1000, 2500	Zn
100	5000	Cu (added to all standards)

Iron

% w_a/w_m[a] in sample	mg/L in solution	elements
0, 0.05, 0.1, 0.2	0, 2.5, 5	As, B, P, Zr
0, 0.05, 0.1, 0.2, 0.5	0, 2.5, 5, 10, 25	Co, Cu, Nb, Ta, V, W
0, 0.2, 0.5, 1.0, 2.0	0, 5, 25, 50, 100	Al, Mn, Si
0, 0.5, 1.0, 2.0, 5.0	0, 25, 50, 100, 250	Mo, Ti
0, 1, 5, 10, 20	0, 50, 250, 500, 1000	Cr, Ni
100	5000	Fe (added to all standards)

Aluminum

% w_a/w_m[a] in sample	mg/L in solution	elements
0, 0.05, 0.1	0, 0.5, 1	Cr, P, Sb, Sn
0, 0.05, 0.1, 0.2, 0.5	0, 0.5, 1, 2, 5	Fe, Pb
0, 0.2, 0.5, 1.0, 2.0	0, 2, 5, 10, 20	Mn, Ni
0, 1, 2, 5, 10	0, 10, 20, 50, 100	Cu, Zn
0, 2, 5, 10, 25	0, 20, 50, 100, 250	Mg
100	1000	Al (added to all standards)

Multielement Standards

Copper based alloys

standard #	element	mg/L solution	% w_a/w_m in solid
1	Cu	5000	100
2	Cu	5000	100
	Zn	2500	50
3	Cu	5000	100
	Ag	5	0.1
	Pb	250	5.0
	Sn	50	1.0
4	Cu	5000	100
	Al	250	5.0
	Fe	10	0.2
	Mn	5	0.1
	Ni	5	0.1
5	Cu	5000	100
	As	5	0.1
	Cd	5	0.1
	P	5	0.1
	Sb	5	0.1
	Si	5	0.1

Iron based alloys

standard #	element	mg/L solution	% w_a/w_m in solid
1	Fe	5000	100
2	Fe	5000	100
	Cr	1000	20
	Cu	100	2.0
	Mn	100	2.0
	Ni	1000	20
3	Fe	5000	100
	Al	100	2.0
	Co	100	2.0
	Mo	100	2.0
	Ti	100	2.0
4	Fe	5000	100
	Nb	10	0.2
	Ta	10	0.2
	V	10	0.2
	W	10	0.2
	Zr	10	0.2
5	Fe	5000	100
	As	10	0.2
	B	10	0.2
	P	10	0.2
	Si	10	0.2

Aluminum based alloys

standard #	element	mg/L solution	% w_a/w_m in solid
1	Al	1000	100
2	Al	1000	100
	Cu	100	10
	Si	100	10
3	Al	1000	100
	Zn	100	10
4	Al	1000	100
	Mg	100	10
	Ni	100	10
5	Al	1000	100
	Cr	10	1
	Fe	10	1
	Mn	10	1
	Pb	10	1
	Sb	10	1
	Sn	10	1
	Ti	10	1
	Zr	10	1

[a] Weight of analyte elements/weight of matrix elements.

B'_i is the uncorrected concentration ratio, B_k is the concentration ratio of the interfering element and K_{ik} is the empirically determined interference factor:

$$B_i = B'_i - \sum_k K_{ik} B_k \tag{6}$$

These empirical interference factors are determined subsequent to the calibration routine and are applied automatically by the central processor prior to the output of the determined concentration ratios.

Interference corrections from the matrix element do not have to be determined empirically since the instrument is standardized by Equation 3, which automatically relates the concentration of the matrix element to the intensity ratio.

Instrumentation. A Model 96-986 (Jarrell-Ash Division, Fisher Scientific Company, Waltham, Mass. 02154) ICAP AtomComp Direct Reading Spectrometer programmed for the elements listed in Table I was used for this study. Automatic background correction provided by a Model 90-555 Spectrum Shifter attachment (Jarrell-Ash) was used for the lines designated in Table I. Lines not programmed into the unit were measured with a Model 96-978 N+1 Channel, a 0.5-m Ebert scanning monochromator (Jarrell-Ash). The operating conditions for the ICAP and spectrometers are shown in Table II.

Reagents. Stock calibration standards containing 1% w/v of the analyte were prepared from spectroscopically pure chemicals (Specpure grade, Johnson Matthey Co. Ltd., England) dissolved in high purity acids (Hipure grade, Fisher Scientific Co., Fair Lawn, N.J.). The same high purity acids were used to dissolve the samples.

Method. *Copper-Based Alloys.* About 250 mg of sample (usually chips or turnings) was transferred to a 2-oz plastic bottle. One milliliter of concentrated nitric acid was added. After the reaction subsided, 15 mL of concentrated hydrochloric acid was

Table IV. Correction Factors (K_{ik}) for Spectral Interferences

	element	interferent	factor
copper alloys	As	Al	0.00467
		Fe	0.00044
	P	Fe	0.87841
	Pb	Al	−0.00100
	Sb	Mn	0.00074
		Al	0.00199
		Pb	0.00417
		Fe	0.00112
		Zn	0.00016
	Sn	Zn	0.00200
iron alloys	Al	Mn	0.00086
		Mo	0.00731
		Co	−0.00640
		V	0.00579
	As	Mo	0.00091
		Ni	0.00085
		Cr	0.00088
		Al	0.00467
		W	−0.04979
		V	0.00142
	Co	Mo	−0.00258
		Ni	0.00004
		Cr	0.00021
		Ti	0.00164
	Cr	Ti	0.00018
		W	0.00102
		V	−0.00019
	Cu	Mo	0.00038
	Mn	Ni	0.00001
	Nb	Ni	−0.00010
		Cr	−0.00015
		Ti	0.06745
		V	0.00801
	Ni	Co	−0.00146
	P	Mo	0.00585
		Ni	0.00025
		Cr	−0.00258
		Cu	0.07717
	Si	Cr	−0.00856
	Ta	Ti	0.00158
		W	0.01358
		Co	0.01357
	Ti	Cr	0.00020
	V	Mo	−0.01069
		Cr	0.00010
		Ti	0.00049
	W	Mo	0.00053
		Cr	0.00007
		Cu	−0.01002
		V	−0.00167
	Zr	Mo	0.00050
		Ni	−0.00007
aluminum alloys	Sb	Mg	0.00013
		Ni	0.00635
		Cu	0.00226
	Zn	Ni	0.00307
	Sn	Zr	0.00200

Table V. Detection Limits (% w/w) for Alloying Elements

	matrix		
element	copper	iron	aluminum
Ag	0.0005	–[a]	–[a]
Al	0.0005	0.0003	–[b]
As	0.0004	0.0006	–
B	–[a]	0.001	–
Cd	0.0001	–	–
Co	–	0.0002	–
Cr	–	0.0002	0.0004
Cu	–[b]	0.0001	0.0003
Fe	0.0006	–[b]	0.0005
Mg	–	–	0.016
Mn	0.0001	0.0001	0.0001
Mo	–	0.0006	–
Nb	–	0.0004	–
Ni	0.0002	0.0004	0.0009
P	0.003	0.002	–
Pb	0.0009	–	0.004
Sb	0.0008	–	0.004
Si	0.0003	0.0003	–
Sn	0.0008	–	0.009
Ta	–	0.005	–
Ti	–	0.0001	0.0002
V	–	0.0004	–
W	–	0.0005	–
Zn	0.003	–	0.0003
Zr	–	0.0003	0.0003

[a] Element not determined. [b] Matrix element.

Table VI. Effect of Weight of Sample upon Measured Concentration Ratios for NBS SRM 1100[a]

element ratio	50	100	150	200	250[b]	300	350	400	500
Ag/Cu	0.992	0.989	0.993	0.997	1.000	0.999	1.006	1.008	1.004
	0.010	0.023	0.008	0.009	0.010	0.005	0.009	0.008	0.006
As/Cu	0.777	0.963	0.989	0.981	1.000	1.008	0.998	1.019	1.023
	0.085	0.047	0.024	0.025	0.013	0.032	0.018	0.027	0.021
Cd/Cu	1.016	1.005	1.002	1.002	1.000	0.997	0.991	0.992	0.997
	0.015	0.028	0.011	0.013	0.013	0.012	0.012	0.014	0.009
Fe/Cu	1.022	0.996	0.995	0.998	1.000	0.996	0.991	1.001	1.005
	0.015	0.018	0.007	0.013	0.012	0.013	0.011	0.018	0.013
Mn/Cu	1.046	0.996	0.997	0.994	1.000	0.998	0.991	0.995	1.003
	0.013	0.017	0.007	0.012	0.013	0.013	0.012	0.018	0.010
Ni/Cu	0.989	0.982	0.999	0.995	1.000	0.998	0.990	0.994	0.994
	0.010	0.020	0.007	0.013	0.015	0.012	0.013	0.013	0.009
Pb/Cu	1.01	1.06	1.03	1.04	1.00	0.95	0.95	1.02	0.97
	0.06	0.09	0.06	0.04	0.06	0.08	0.05	0.04	0.05
Sn/Cu	0.85	0.97	0.98	1.01	1.00	0.97	0.98	1.02	1.01
	0.07	0.03	0.09	0.06	0.05	0.08	0.07	0.03	0.02
Zn/Cu	1.060	1.008	1.004	0.996	1.000	1.002	0.985	0.998	0.990
	0.010	0.044	0.012	0.014	0.010	0.012	0.008	0.012	0.010

[a] Weight (mg) in 50-mL solution. [b] Normalization value.

Table VII. Copper Based Alloys (Values in % w/w)

SRM no.	type		Ag	Al	As	Cd	Cu	Fe	Mn
1100	cartridge	NBS	0.019	0.008	0.019	0.013	67.43	0.072	0.003
	brass	ICAP	0.018	0.010	0.019	0.0136	67.3	0.068	0.0031
		limits	0.001	0.002	0.001	0.0004	0.4	0.004	0.0003
1101	cartridge	NBS	0.003	0.0006	0.009	0.0055	69.50	0.037	0.0055
	brass	ICAP	0.0026	0.004	0.008	0.0060	69.2	0.036	0.0057
		limits	0.0008	0.002	0.001	0.0003	0.3	0.002	0.0002
1104	free cutting	NBS	-	-	-	-	63.33	0.088	-
	brass	ICAP	<0.0005	0.003	0.0006	<0.0001	61.5	0.088	<0.0001
		limits	-	0.002	0.0004	-	0.2	0.002	-
1105	free cutting	NBS	-	-	-	-	63.7	0.044	-
	brass	ICAP	<0.0005	0.006	0.0010	0.0006	63.7	0.042	0.0001
		limits	-	0.001	0.0005	0.0001	0.1	0.002	0.0001
1106	naval brass	NBS	-	-	-	-	59.08	0.004	0.005
		ICAP	<0.0005	0.012	<0.0004	0.0011	59.3	0.006	0.0046
		limits	-	0.002	-	0.0001	0.3	0.002	0.0004
1108	naval brass	NBS	-	-	-	-	64.95	0.050	0.025
		ICAP	<0.0005	0.046	<0.0004	<0.0001	65.0	0.049	0.025
		limits	-	0.003	-	-	0.1	0.002	0.001
1110	red brass	NBS	-	-	-	-	84.59	0.033	-
		ICAP	0.0011	0.0007	<0.0004	0.0003	84.6	0.032	0.0001
		limits	0.0006	0.0005	-	0.0001	0.1	0.002	0.0001
1114	gilding metal	NBS	-	-	-	-	96.45	0.017	-
		ICAP	0.0009	<0.0005	<0.0004	<0.0001	96.46	0.017	0.0001
		limits	0.0005	-	-	-	0.05	0.002	0.0001
1115	commercial	NBS	-	-	-	-	87.96	0.13	-
	brass	ICAP	0.0018	0.0008	<0.0004	<0.0001	88.0	0.130	<0.0001
		limits	0.0006	0.0005	-	-	0.1	0.001	-
1118	aluminum	NBS	-	2.80	0.007	-	75.1	0.065	-
	bronze	ICAP	<0.0005	2.78	0.0065	0.0001	75.3	0.064	0.0001
		limits	-	0.02	0.0007	0.0001	0.2	0.004	0.0001

SRM no.	type		Ni	P	Pb	Sb	Si	Sn	Zn
1100	cartridge	NBS	0.052	0.010	0.106	0.018	(0.010)	0.055	32.20
	brass	ICAP	0.0524	0.012	0.103	0.017	0.0087	0.053	32.4
		limits	0.0008	0.003	0.003	0.001	0.0005	0.002	0.4
1101	cartridge	NBS	0.013	0.002	0.050	0.012	(0.005)	0.016	30.30
	brass	ICAP	0.0131	<0.003	0.050	0.012	0.0047	0.017	30.6
		limits	0.0005	-	0.002	0.001	0.0002	0.001	0.3
1104	free cutting	NBS	0.070	0.005	2.77	-	-	0.43	35.3
	brass	ICAP	0.070	0.008	2.72	<0.0008	0.0008	0.430	35.3
		limits	0.003	0.004	0.05	-	0.0003	0.006	0.2
1105	free cutting	NBS	0.043	0.003	2.0	-	-	0.21	34.0
	brass	ICAP	0.044	0.003	1.96	<0.0008	0.0012	0.211	34.1
		limits	0.001	0.003	0.03	-	0.0004	0.006	0.1
1106	naval brass	NBS	0.025	-	0.032	-	-	0.74	40.08
		ICAP	0.0250	<0.003	0.032	<0.0008	0.0010	0.743	39.9
		limits	0.0007	-	0.002	-	0.0004	0.009	0.2
1108	naval brass	NBS	0.033	-	0.063	-	-	0.39	34.42
		ICAP	0.031	<0.003	0.066	<0.0008	0.0004	0.394	34.40
		limits	0.001	-	0.002	-	0.003	0.008	0.08
1110	red brass	NBS	0.053	-	0.033	-		0.051	15.20
		ICAP	0.052	<0.003	0.033	<0.0008	<0.0003	0.050	15.2
		limits	0.002	-	0.001	-	-	0.002	0.2
1114	gilding metal	NBS	0.021	0.009	0.012	-	-	0.027	3.47
		ICAP	0.0208	0.009	0.008	<0.0008	<0.0003	0.028	3.47
		limits	0.0007	0.003	0.002	-	-	0.001	0.05
1115	commercial	NBS	0.074	0.005	0.013	-	-	0.10	11.73
	brass	ICAP	0.074	0.005	0.014	<0.0008	<0.0003	0.103	11.6
		limits	0.002	0.003	0.001	-	-	0.002	0.2
1118	aluminum	NBS	-	0.13	0.025	0.010	0.0021	-	21.9
	bronze	ICAP	0.0005	0.129	0.019	0.008	0.0020	<0.0008	21.8
		limits	0.0003	0.009	0.006	0.002	0.0007	-	0.1

Statistical Analysis of Data

	Cu	Fe	Ni	P	Pb	Zn
n	10	10	9	6	10	10
m	0.9990	1.001	0.999	0.996	9.994	1.0003
b	0.1119	−0.0004	−0.0001	0.0008	0.0003	−0.0119
r	1.0000	0.9997	0.9992	0.9982	0.9994	1.0000
χ^2	0.78	0.85	1.28	0.17	2.47	1.12
p	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
t	0.41	−1.55	0.75	1.40	−1.13	0.36
p	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

Table VIII. Iron and Steel (Values in % w/w)

SRM no.	type		Al	As	B	Co	Cr	Cu
8i	plain	NBS	-	-	-	-	0.009	0.016
	carbon	ICAP	<0.0003	<0.0006	<0.001	<0.0002	0.0072	0.0136
		limits	-	-	-	-	0.0006	0.0006
19g	plain	NBS	0.031	-	-	0.012	0.374	0.093
	carbon	ICAP	0.030	<0.0006	<0.001	0.0109	0.377	0.093
		limits	0.004	-	-	0.0005	0.009	0.002
51b	plain	NBS	-	-	-	-	0.455	0.071
	carbon	ICAP	0.010	<0.0006	<0.001	<0.0002	0.455	0.072
		limits	0.001	-	-	-	0.008	0.002
65d	plain	NBS	0.059	-	-	-	0.049	0.051
	carbon	ICAP	0.058	<0.0006	<0.001	0.0054	0.049	0.050
		limits	0.003	-	-	0.0003	0.001	0.001
160a	stainless	NBS	-	-	-	0.071	18.74	0.174
	steel	ICAP	<0.0003	<0.0006	<0.001	0.067	18.6	0.175
		limits	-	-	-	0.002	0.2	0.002
344	high	NBS	1.16	-	-	-	14.95	0.106
	alloy	ICAP	1.16	<0.0006	<0.001	0.0591	15.04	0.105
		limits	0.01	-	-	0.0004	0.04	0.002
348	high	NBS	0.23	-	0.0031	-	14.54	0.22
	alloy	ICAP	0.226	<0.0006	0.003	0.127	14.54	0.219
		limits	0.004	-	0.001	0.001	0.05	0.002
1261	low	NBS	0.021	0.017	0.0005	0.030	0.69	0.042
	alloy	ICAP	0.022	0.017	<0.001	0.0302	0.690	0.042
		limits	0.002	0.002	-	0.0007	0.006	0.002
1262	low	NBS	0.095	0.092	0.0025	0.30	0.30	0.50
	alloy	ICAP	0.093	0.091	0.003	0.311	0.305	0.499
		limits	0.005	0.005	0.001	0.005	0.005	0.006
1263	low	NBS	0.24	0.010	0.00091	0.048	1.31	0.098
	alloy	ICAP	0.242	0.010	<0.001	0.046	1.31	0.098
		limits	0.008	0.002	-	0.001	0.01	0.002
1264	low	NBS	(0.008)	0.052	0.011	0.15	0.065	0.249
	alloy	ICAP	0.008	0.050	0.011	0.154	0.065	0.249
		limits	0.002	0.003	0.002	0.004	0.003	0.004
1265	electrolytic	NBS	(0.0007)	(0.0002)	0.00013	0.0070	0.0072	0.0058
	iron	ICAP	0.0005	<0.0006	<0.001	0.0068	0.0072	0.0058
		limits	0.0004	-	-	0.0004	0.0008	0.0007

SRM no.	type		Fe	Mn	Mo	Nb	Ni	P
8i	plain	NBS	-	0.511	0.003	-	0.009	0.080
	carbon	ICAP	99.18	0.515	0.004	<0.0004	0.010	0.081
		limits	0.01	0.006	0.001	-	0.001	0.009
19g	plain	NBS	-	0.554	0.013	0.026	0.066	0.046
	carbon	ICAP	98.29	0.555	0.012	0.0280	0.067	0.048
		limits	0.02	0.004	0.001	0.0008	0.003	0.008
51b	plain	NBS	-	0.573	0.014	-	0.053	0.013
	carbon	ICAP	97.32	0.574	0.014	<0.0004	0.054	0.014
		limits	0.02	0.006	0.001	-	0.002	0.004
65d	plain	NBS	-	0.073	0.025	-	0.060	0.015
	carbon	ICAP	98.35	0.071	0.025	<0.0004	0.060	0.017
		limits	0.02	0.006	0.002	-	0.001	0.004
160a	stainless	NBS	-	1.62	2.83	-	14.13	0.027
	steel	ICAP	61.7	1.62	2.84	0.010	14.18	0.031
		limits	0.2	0.01	0.04	0.001	0.09	0.004
344	high	NBS	-	0.57	2.40	-	7.28	0.018
	alloy	ICAP	72.76	0.567	2.41	0.004	7.31	0.014
		limits	0.03	0.005	0.03	0.001	0.02	0.004
348	high	NBS	53.3	1.48	1.3	-	25.8	0.015
	alloy	ICAP	53.28	1.481	1.30	0.020	25.73	0.014
		limits	0.09	0.007	0.01	0.002	0.08	0.004
1261	low	NBS	(95.6)	0.66	0.19	0.022	1.99	0.015
	alloy	ICAP	95.54	0.662	0.189	0.021	1.99	0.015
		limits	0.02	0.005	0.004	0.001	0.02	0.003
1262	low	NBS	(95.3)	1.04	0.068	0.29	0.59	0.042
	alloy	ICAP	95.74	1.05	0.069	0.078	0.59	0.044
		limits	0.02	0.01	0.005	0.008	0.01	0.009
1263	low	NBS	(94.4)	1.50	0.030	0.049	0.32	0.029
	alloy	ICAP	94.48	1.51	0.030	0.048	0.324	0.028
		limits	0.02	0.01	0.002	0.002	0.005	0.005
1264	low	NBS	(96.7)	0.255	0.49	0.157	0.142	0.018
	alloy	ICAP	96.75	0.255	0.49	0.157	0.142	0.018
		limits	0.02	0.005	0.01	0.008	0.002	0.003
1265	electrolytic	NBS	(99.9)	0.0057	0.0050	<0.00001	0.041	0.0025
	iron	ICAP	99.90	0.0058	0.0051	<0.0004	0.043	0.0039
		limits	0.01	0.0004	0.0008	-	0.002	0.0038

Table VIII. (*Continued*)

SRM no.	type		Si	Ta	Ti[a]	V	W	Zr
8i	plain	NBS	0.020	-	-	0.012	-	-
	carbon	ICAP	0.021	<0.005	<0.0011	0.013	<0.0005	<0.0003
		limits	0.001	-	-	0.002	-	-
19g	plain	NBS	0.186	-	0.027	0.012	-	-
	carbon	ICAP	0.186	<0.005	0.0266	0.013	<0.0005	<0.0003
		limits	0.004	-	0.0008	0.001	-	-
51b	plain	NBS	0.246	-	-	0.002	-	-
	carbon	ICAP	0.245	<0.005	0.0002	0.0019	<0.0005	<0.0003
		limits	0.007	-	0.0001	0.0006	-	-
65d	plain	NBS	0.370	-	-	0.002	-	-
	carbon	ICAP	0.366	<0.005	0.0012	0.0021	0.0008	<0.0003
		limits	0.077	-	0.0003	0.0008	0.0005	-
160a	stainless	NBS	0.605	-	-	0.051	-	-
	steel	ICAP	0.605	<0.005	0.0026	0.043	0.036	<0.0003
		limits	0.008	-	0.0003	0.002	0.002	-
344	high	NBS	0.395	0.002	0.076	0.040	-	-
	alloy	ICAP	0.396	<0.005	0.076	0.0429	0.0010	<0.0003
		limits	0.005	-	0.003	0.0009	0.0005	-
348	high	NBS	0.54	-	2.24	0.25	-	-
	alloy	ICAP	0.541	<0.005	2.24	0.245	0.029	<0.0003
		limits	0.007	-	0.01	0.005	0.002	-
1261	low	NBS	0.223	0.020	0.020	0.011	0.015	0.009
	alloy	ICAP	0.224	0.022	0.0199	0.013	0.018	0.0087
		limits	0.005	0.006	0.0006	0.001	0.001	0.0005
1262	low	NBS	0.39	0.20	0.084	0.041	0.21	0.19
	alloy	ICAP	0.38	0.023	0.038	0.041	0.217	0.194
		limits	0.01	0.004	-	0.002	0.008	0.008
1263	low	NBS	0.74	(0.053)	0.050	0.31	0.045	0.049
	alloy	ICAP	0.726	0.047	0.049	0.312	0.047	0.048
		limits	0.005	0.005	0.002	0.009	0.002	0.001
1264	low	NBS	0.067	0.11	0.24	0.105	0.10	0.068
	alloy	ICAP	0.068	0.091	0.244	0.107	0.101	0.068
		limits	0.002	0.009	0.009	0.002	0.004	0.002
1265	electrolytic	NBS	0.0080	-(<0.00005)	0.0006	0.0006	(-0.00004)	-(<0.00001)
	iron	ICAP	0.0079	<0.005	0.0001	0.0007	<0.0005	<0.0003
		limits	0.0008	-	0.0001	0.0005	-	-

Statistical Analysis of Data

	n	m	b	r	χ^2	p	t	p
Al	7	0.999	0.0001	1.0000	0.14	<0.02	-1.076	<0.02
Co	7	1.005	-0.0007	0.9992	2.90	<0.02	0.219	<0.02
Cr	12	1.0035	-0.0011	1.0000	2.35	<0.02	0.007	<0.02
Cu	12	1.006	-0.0011	0.9999	1.65	<0.02	-0.666	<0.02
Mn	12	1.0019	0.0001	1.0000	0.45	<0.02	1.978	<0.02
Mo	12	1.001	0.0000	1.0000	0.55	<0.02	1.502	<0.02
Ni	12	1.0006	0.0006	1.0000	1.28	<0.02	-0.110	<0.02
P	12	1.026	-0.0002	0.9894	0.61	<0.02	0.891	<0.02
Si	12	0.994	0.0006	0.9999	1.42	<0.02	-0.673	<0.02
Ti[a]	6	1.001	-0.0005	1.0000	0.27	<0.02	-1.334	<0.02
V	12	1.008	0.0004	0.9982	7.53	<0.02	0.111	<0.02

[a] Sample 1262 not used in statistical analysis for this element.

added. The solution was allowed to stand in a water bath at 40 °C for about 5 min until dissolution was complete. Deionized water then was added to bring the final solution volume to about 50 mL, and the solution analyzed using the ICAP.

Iron-Based Alloys. About 250 mg of sample (usually chips or turnings) was transferred to a 50-mL Teflon beaker. Twenty milliliters of aqua regia was added and, after the reaction subsided, the solution was boiled for 20 min. The cooled solution then was diluted to about 50 mL with water and analyzed by the ICAP after undissolved carbon particles were allowed to settle from solution.

Aluminum-Based Alloys. About 100 mg of sample (usually chips or turnings) was transferred to a 250-mL glass beaker. Ten milliliters of 6 M hydrochloric acid was added and the solution heated until no further dissolution occurred (about 15–20 min). At this point, black specks of silicon metal are visible in the solution. The solution then was cooled and diluted to about 100 mL with water, and allowed to stand so that undissolved silicon particles settled from solution before analysis by the ICAP.

Calibration Standards. The instrument was calibrated by using synthetically prepared standards. These were made up to represent original alloys that contained up to 50% of the analyte (relative to the weight of matrix element) in the presence of a constant concentration of the matrix element. The calibration range for each element in each matrix is shown in Table III. After the linearity of every analytical line investigated was established to be over the range shown in Table III, the instrument was standardized using the low standard and the high standard. In order to reduce the number of standard solutions required to calibrate the unit for routine operation, the multielemental standards listed in Table III were used.

Following instrument standardization, the empirical interference correction factors (K_{ik}) were determined. This was achieved by introducing the high, single element calibration standard into the ICAP and observing the apparent concentration of the affected analytes. The factors found to be significant at the analyte and interferent levels in the original samples are shown in Table IV. These factors were stored in the data processing unit and used to modify the apparent concentration ratios determined from the calibration curve into the "real" concentration ratios using Equation 6.

Concentration Calculations. Because the elements left undetermined in the copper alloys constituted less than 0.01% of the

Table IX. Aluminum Alloys (Values in % w/w)

BCS no.	type		Cr	Cu	Fe	Mg	Mn	Ni
181/2	copper	BCS	(0.008)	3.96	0.42	1.56	0.20	1.90
	aluminum	ICAP	0.0079	3.96	0.42	1.57	0.201	1.89
	alloy	limits	0.0008	0.03	0.01	0.02	0.006	0.03
182/2	silicon	BCS	-	0.045	0.47	0.075	0.21	0.055
	aluminum	ICAP	<0.0005	0.042	0.45	0.075	0.207	0.055
	alloy	limits	-	0.001	0.01	0.02	0.006	0.002
216/2	duralumin	BCS	-	4.56	0.28	0.75	0.71	0.17
	alloy	ICAP	0.0008	4.44	0.28	0.73	0.71	0.166
		limits	0.0005	0.06	0.01	0.02	0.02	0.004
262/2	magnesium	BCS	(0.002)	0.039	0.20	10.74	0.084	0.071
	aluminum	ICAP	0.0019	0.040	0.20	10.68	0.083	0.073
	alloy	limits	0.0006	0.001	0.02	0.09	0.002	0.002
263/2	magnesium	BCS	0.074	0.019	0.26	4.67	0.36	-
	aluminum	ICAP	0.075	0.019	0.263	4.69	0.354	0.0015
	alloy	limits	0.002	0.002	0.008	0.06	0.007	0.0009
268	silicon	BCS	-	1.34	0.39	0.56	0.22	0.12
	aluminum	ICAP	<0.0005	1.35	0.397	0.57	0.217	0.122
	alloy	limits	-	0.02	0.009	0.02	0.006	0.004
300/1	zinc	BCS	0.13	1.27	0.24	2.74	0.33	-
	aluminum	ICAP	0.133	1.26	0.241	2.72	0.329	0.0012
	alloy	limits	0.003	0.03	0.006	0.07	0.008	0.0008
380	aluminum	BCS	-	0.90	1.15	0.18	0.018	0.91
	alloy	ICAP	<0.0005	0.91	1.16	0.19	0.020	0.911
		limits	-	0.01	0.03	0.02	0.002	0.008

BCS no.	type		Pb	Sb	Sn	Ti	Zn	Zr
181/2	copper	BCS	0.040	-	0.028	0.019	0.074	-
	aluminum	ICAP	0.040	<0.004	0.027	0.0186	0.0739	<0.0003
	alloy	limits	0.004	-	0.009	0.0004	0.0009	-
182/2	silicon	BCS	0.050	-	0.025	0.11	0.100	-
	aluminum	ICAP	0.052	<0.004	0.028	0.109	0.095	<0.0003
	alloy	limits	0.004	-	0.009	0.001	0.003	-
216/2	duralumin	BCS	0.038	0.029	0.048	0.037	0.20	-
	alloy	ICAP	0.036	0.030	0.048	0.037	0.203	<0.0003
		limits	0.006	0.005	0.009	0.003	0.003	-
262/2	magnesium	BCS	(0.054)	-	(0.042)	0.005	0.084	-
	aluminum	ICAP	0.049	<0.004	0.035	0.0043	0.086	<0.0003
	alloy	limits	0.006	-	0.009	0.0004	0.007	-
263/2	magnesium	BCS	-	-	-	0.022	0.056	-
	aluminum	ICAP	<0.004	<0.004	<0.005	0.0225	0.056	<0.0003
	alloy	limits	-	-	-	0.0009	0.001	-
268	silicon	BCS	0.035	-	0.03	<0.02	0.05	-
	aluminum	ICAP	0.035	<0.004	0.033	0.0157	0.052	<0.0003
	alloy	limits	0.005	-	0.006	0.0005	0.003	-
300/1	zinc	BCS	-	-	-	0.09	5.87	0.18
	aluminum	ICAP	0.012	<0.004	<0.005	0.09	5.88	0.181
	alloy	limits	0.005	-	-	0.001	0.09	0.004
380	aluminum	BCS	-	-	-	0.22	0.011	-
	alloy	ICAP	<0.004	<0.004	<0.005	0.222	0.0108	<0.0003
		limits	-	-	-	0.02	0.0008	-

Statistical Analysis of Data

	Cu	Fe	Mg	Mn	Ni	Ti	Zn
n	8	8	8	8	6	7	8
m	0.998	0.992	0.997	0.982	0.997	1.006	0.998
b	−0.0008	0.0019	0.0026	0.0022	0.0010	−0.0005	−0.0000
r	0.9998	0.9982	0.9999	0.9998	1.0000	0.9999	0.9999
χ^2	3.42	1.30	0.58	0.60	0.16	0.75	0.69
p	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
t	−0.855	0.000	−0.699	−0.693	−0.690	−0.926	0.553
p	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

alloy, the final concentration calculations were performed on-line by the central processing unit, and direct concentration values were printed out. For the iron- and aluminum-based alloys, the concentration ratios only were printed. Final concentration calculations were performed off-line after concentrations of elements not determined above 0.02% (C_j values) had been merged with the ICAP data. In this study, values for carbon, sulfur, and nitrogen in iron-based alloys, and silicon in aluminum alloys were taken from the certificates of analysis supplied by NBS and BAS, respectively.

Effect of Sample Weight. In order to determine the effect of different sample weights, samples of NBS SRM 1100 Cartridge Brass were weighed on a milligram balance over the range 50–500 mg into Teflon beakers. Each sample then was treated with 1 mL of concentrated nitric acid and, after the reaction subsided, 15 mL of concentrated hydrochloric acid was added. After dissolution, the solutions were transferred to 50-mL Teflon volumetric flasks, diluted to volume with water, and analyzed by the ICAP.

RESULTS AND DISCUSSION

Detection Limits. The experimentally-determined detection limits for the copper, iron, and aluminum matrices analyzed are listed in Table V. The detection limits are defined as the concentration of analyte required to produce a signal equivalent to the 95% confidence limit (2.131 standard deviation) of the background variation as determined on a set of 16 measurements performed on the matrix blank interspersed randomly among the samples analyzed. Although the variation of detection limits with sample weight was not studied here, the confidence limits measured for the analysis of sample 1265, a high purity iron, are close to the detection limits measured on the blank iron standard.

Effect of Sample Weight Analyzed. The effect of sample weight on the determined concentration ratios of several elements in NBS SRM 1100 Cartridge Brass is shown in Table VI. The results normalized against the 250-mg sample in 50-mL value, are expressed as the mean and the 95% confidence level on a set of eight replicates at each solute concentration. Clearly, there is no significant difference in the determined concentration ratio for weights in the 150–500 mg range which represents the equivalent of a 40% weighing error. In practice, we decided to limit the weighing error to about ±20% by using a milligram balance to ensure a minimum sample size of 200 mg and a maximum sample size of 300 mg.

The volume error was kept to about ±10% by use of graduated glass beakers. When plastic containers were used, a simple batch calibration was performed by dispensing 50 mL of water from a graduate and marking a line on the outside of the container.

Copper-Based Alloys. Analytical data obtained from the analysis of NBS reference copper-based alloys including brasses, bronzes, and gilding metals are listed in Table VII. The ICAP values are expressed as the mean of a set of 16 replicate analyses for each element plus or minus the 95% confidence limit. In addition, for each element certified to be present in at least six alloys, the correlation coefficient, slope and intercept of the linear regression line of the form of Equation 7 between the NBS certified values and the experimentally determined ICAP values, weighted with respect to the 95% confidence limit for the determination, are shown:

$$(\mathrm{ICAP}) = m(\mathrm{NBS}) + b \tag{7}$$

Both the chi-square value for the regression line and the Students' "t" value for the paired data points are consistent with the 98% confidence limit, indicating a lack of bias between the ICAP and the certified values.

Iron-Based Alloys. Analytical data obtained from 12 NBS reference iron and steel samples determined by the ICAP are listed in Table VIII. These data are expressed as the mean of the number of at least 16 replicate analyses for each sample together with the 95% confidence limit for each elemental determination. Analyses for carbon, nitrogen, and sulfur in these samples were taken from the NBS certificate prior to calculation of the final concentration for each element.

The statistical data tabulated for the iron-based alloy samples are determined in the same manner as were those for the copper-based alloys. The ICAP data were found to show no significant deviation ($p < 0.02$) from the referee data with the exception of sample 1262. It is believed that the low ICAP values from these samples are caused by the presence of niobium and titanium in the sample as carbides which are insoluble by this technique. The residue from the dissolution of sample 1262 analyzed by a dc arc in conjunction with a Mark IV 3.4-m Ebert Spectrograph (Jarrell-Ash) showed that high levels of niobium and titanium were present. Furthermore, calibration curves obtained for samples 1261–1265 using an electronically-controlled waveform spark source coupled to a Model 90-750 AtomComp Direct Reading Spectrometer (Jarrell-Ash) indicated that these elements were present in the sample at the certified values.

Aluminum-Based Alloys. Analytical data obtained from the determination of eight BCS aluminum alloys using the ICAP technique are shown in Table IX. Prior to calculation of the elemental concentration C_i from the determined concentration ratios, the silicon concentrations (C_j) listed on the certification of analysis sheet were used to solve Equation 2 for the aluminum concentration (C_M).

The statistical analyses presented in Table IX show that there is no significant difference ($p < 0.02$) between the ICAP data and the certified values.

CONCLUSIONS

The direct reading ICAP spectrometer coupled with the concentration ratio method of analysis has been demonstrated to produce analytically accurate data for the determination of alloying elements in metals. This is true over a concentration range exceeding four decades with a typical precision of better than 10% for trace and 1% for minor and major alloying components. The relative freedom from chemical interferences eliminates the matching of standards to samples that is required in other analytical techniques. Indeed, the only matrix matching required is the addition of the matrix element and acids to the calibration standards. With such minimal matching, it is possible to analyze samples in which the major matrix element extends over a wide range. The use of the concentration ratio procedure also permits significant dilution errors from the target dilution factor without any resultant loss of analytical accuracy. This permits very rapid sample preparation that requires a minimum of operator skill. Indeed, the tolerance of the procedure to dilution errors suggests that the automating of the entire sample preparation procedure might be practically and economically feasible.

The limitations of the concentration ratio method are that all elements present in significant concentrations (total nonanalyzed elements should not exceed 0.1%) must be determined and that insoluble materials could produce a significant error. Furthermore, any error caused by insoluble material is compounded over all elements. However, only one among the 30 samples analyzed in this study exhibited this problem. In this case, the only significant errors observed were on those elements that had been incompletely dissolved.

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