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The Spectrographic Determination of Impurities in Copper-base Samples of Small Dimensions*

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Serious problems arise in the point-to-point spectrographic analysis of copper-base materials if only wire or thin-sheet samples are available. In the procedure recommended in this paper, the sample is converted into oxide, transferred to a graphite cup of optimum dimensions, then examined spectrographically. Standard oxide samples are prepared in a similar way (from high-purity reagents) and excited, and resulting reference spectra are used to evaluate the impurities in copper, brass, phosphor and aluminium bronze, cupro-nickel, nickel-silver and Everdur. Densities of the recommended impurity lines for each of these materials are in remarkably close agreement at all comparable impurity levels.

The validity of the proposed method has been substantiated by a comparison with similar analytical results obtained by alternative, often time-consuming, procedures.

A wide range of impurities, down to about the 10 p.p.m. level, can be determined in a single sample within 90 minutes, and several samples can be analysed concurrently.

IN direct point-to-point spectrographic analysis, the provision of a uniformly large (massive) single-piece sample is essential. Serious problems arise if wire or thin-sheet samples are used, because undissipated heat accumulates within the sample when it is excited. The significance of this is that some impurities volatilise more rapidly than others, and the rate of volatilisation can be neither predicted nor controlled.

Alternative methods of determining most of the impurities in these small samples are time-consuming, and experiments were designed to overcome the problems encountered when these materials are analysed spectrographically.

In the following experimental work, a BNF General-purpose Source Unit was used unless otherwise stated.

EXPERIMENTAL

SAMPLE PREPARATION—

Several methods of preparing suitable samples of wire and thin sheet for spectrographic examination were examined.

PROVISION OF COMPACTS—

Attempts were made to pressure-weld the sample, and to establish optimum punch and die sizes and pressing loads, but these tests were not successful because all of the samples were seriously contaminated with iron and disintegrated on excitation.

EXAMINATION OF SOLUTIONS—

The use of a spectrographic solution method has two outstanding advantages, *viz.*, standards can readily be prepared from high-purity reagents, and the standards and samples are converted into a common matrix.

One expected source of interference in such a method is the OH-band spectrum produced in the region of the bismuth 306·7 nm line by aqueous solutions, and tests in which the "polyethylene-cup" method[1] was used confirmed this. In an attempt to eliminate all water from the solution before excitation, a micro-Bunsen flame was directed between the pick-up

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and excitation regions of a rotating graphite-disc electrode, but this modification failed to achieve the desired effect.

A high-frequency plasma jet can be used to replace the conventional spectrographic discharge; a solution of the sample is nebulised directly into the plasma, and resulting spectra usually have relatively high-density and low-background characteristics. All tests with this alternative source of excitation (by the courtesy of Mr. S. Greenfield, Messrs. Albright & Wilson) failed to eliminate the OH-band spectrum, even after stringent drying of the plasma gas that was thought to be the primary source of OH-band radiation.

OXIDE - RESIN METHOD—

This is a standard method of spectrographic analysis, in which the sample, in the form of an oxide powder, is mixed with a Bakelite resin and the cured mixture is excited in the crater of a graphite-rod electrode.[2]

When this method was applied to an essentially copper matrix, the sensitivities obtained for some elements were poor.

OXIDE POWDER - CUP PROCEDURE—

In subsequent tests the oxide powder alone was excited in a series of graphite cups of different dimensions, and trial exposures indicated that the method is inherently both sensitive and reproducible; however, cup dimensions were critical. Small cups became very hot and produced a high-background continuum, and when relatively large cups were used the discharge concentrated on the oxide sample, reducing it to the metal, and sensitivities and reproducibilities were poor.

When a graphite cup of the dimensions referred to under Method was used, the discharge circled the lip of the cup, the oxide was drawn directly into the discharge by the vacuum formed and sensitivities and reproducibilities were good.

In further tests to establish the most suitable weight of oxide and optimum excitation conditions to use, it was shown to be a disadvantage to press the oxide firmly into the cup. When the oxide was uniformly distributed within the crater, by lightly tapping the cup, even better reproducibilities and sensitivities were obtained.

Subsequent experimental work was based on the experience gained with this oxide powder - cup procedure in these preliminary tests.

PREPARATION OF REFERENCE SOLUTIONS—

It was necessary to provide a series of reference solutions typical of those obtained when copper and certain copper alloys are dissolved in a convenient solvent. Each solution was evaporated to dryness and the residue converted into oxide before applying the method so far developed.

For our immediate purposes, impurities in the following materials were of interest: copper; brasses (Cu 60 and 80 per cent., Zn 40 and 20 per cent.); phosphor bronze (Cu 95, Sn 4·8 and P 0·2 per cent.); aluminium bronze (Cu 90 and Al 10 per cent.); cupro-nickel (Cu 75 and Ni 25 per cent.); nickel-silver (Cu 60, Ni 15 and Zn 25 per cent.); and Everdur (Cu 96, Si 3 and Mn 1 per cent.).

Individual standard solutions were prepared in such a way that when composite solutions were evaporated and the residues were converted into oxides, the dry residues contained the equivalent of 0·5 g of the sample *plus* 0, 10, 50 or 100 p.p.m., 0·05, 0·10, 0·20, 0·30 or 0·50 per cent. of a selection of impurities.

For example, in preparing one of the 60/40 brass standards (see Method), to 6·0 ml of the standard copper solution A were added 4·0 ml of the standard zinc solution B and 3·0 ml of each of the undiluted standard solutions F, G, H, I, J and K. In this way, an oxide was ultimately prepared simulating the composition of the oxide that would be obtained from a 60/40 brass sample containing 0·3 per cent. of each of the following impurities: silver, bismuth, aluminium, manganese, iron, lead, nickel, arsenic, antimony, silicon, tin and phosphorus.

Other standard oxides in the same series were prepared in a similar way; the volumes of the standard copper and zinc solutions were the same but, instead of 3·0 ml of each of the standard solutions F, G, H, I, J and K, equal volumes of each of these solutions (before or after the prescribed dilutions) were used to provide the individual impurities referred to earlier.

This provided nine standard oxides (including a blank) for this particular 60/40 brass series, and similar standard oxides were prepared for each of the other six materials.

Some of the reagents used in preparing the standard solutions dissolved more rapidly in hydrochloric acid than in any other solvent, but tests on the oxide residue from a series of simulated brass (60/40) samples showed that if a large amount of chloride was present, there was a significant loss of arsenic; other impurities were not affected. The use of hydrochloric acid in any stage of the procedure had, therefore, to be circumvented.

Preliminary tests confirmed that none of the elements was lost during conversion of any solution into a dry residue, before excitation, provided the oxides were prepared in accordance with the details given under Method.

EXCITATION OF OXIDES—

The oxides were all examined spectrographically (see Method) and resulting spectra were evaluated visually, and independently, by three analysts.

METHOD

PREPARATION OF STANDARD SOLUTIONS—

Use high-purity reagents and distilled water (including that used for dilutions) throughout.

Copper solution (A)—Dissolve 50 g of copper in 500 ml of dilute nitric acid (1 + 1). Warm the solution gently to expel oxides of nitrogen, cool and dilute to 1 litre.
    1 ml of solution ≡ 50 mg of copper.

Zinc solution (B)—As for copper, but use 50 g of zinc.
    1 ml of solution ≡ 50 mg of zinc.

Nickel solution (C)—As for copper, but use 25 g of nickel.
    1 ml of solution ≡ 25 mg of nickel.

Aluminium solution (D)—As for copper, but use 2·5 g of aluminium, a few milligrams of mercury(I) nitrate and 50 ml of dilute nitric acid (1 + 1); the reaction is vigorous. Cool, and dilute the solution to 100 ml.
    1 ml of solution ≡ 25 mg of aluminium.

Manganese solution (E)—Dissolve 0·5 g of manganese in 10 ml of dilute nitric acid (1 + 1). Warm the solution gently to expel oxides of nitrogen, cool and dilute to 100 ml.
    1 ml of solution ≡ 5 mg of manganese.

Zinc, silver, bismuth, aluminium, manganese, iron, lead and nickel solution (F)—Dissolve 0·5 g of each of these metals separately in about 5 ml of dilute nitric acid (1 + 1); the presence of about 1 mg of mercury(I) nitrate will aid dissolution of the aluminium. Dilute the combined solutions to 1 litre in a calibrated flask.
    1 ml of solution ≡ 0·5 mg of each of the above metals.

Arsenic solution (G)—Dissolve 0·165 g of arsenic(III) oxide (dried at 105 °C) in 10 ml of 10 per cent. w/v sodium hydroxide solution. Acidify the solution to litmus with dilute nitric acid (1 + 1), then add an excess of 5 ml of the dilute acid and dilute to 250 ml.
    1 ml of solution ≡ 0·5 mg of arsenic.

Antimony solution (H)—Dissolve 0·334 g of potassium antimony tartrate (dried at 105 °C) in water and dilute to 250 ml.
    1 ml of solution ≡ 0·5 mg of antimony.

Tin solution (I)—Dissolve 0·5 g of tin in 50 ml of dilute sulphuric acid (1 + 1). Dilute to 100 ml with the same acid.
    1 ml of solution ≡ 5·0 mg of tin.

Phosphorus solution (J)—Dissolve 2·195 g of potassium dihydrogen orthophosphate (dried at 105 °C) in water and dilute to 1 litre.
    1 ml of solution ≡ 0·5 mg of phosphorus.

Silicon solution (K)—Transfer 0·2673 g of calcined silica to a small platinum dish, fuse it with about 1 g of anhydrous sodium carbonate and cool. Dissolve the melt in water, and dilute the solution to 250 ml in a calibrated flask. (It is preferable to make this solution freshly each time it is required, but it can be stored for a few days in a polythene container.)
    1 ml of solution ≡ 0·5 mg of silicon.

In making up some of the standard oxides, to avoid taking an inconveniently small aliquot of each of the individual standard solutions F, G, H, I, J and K, dilute, separately, each of these solutions to provide two independent solutions such that with one of them 1 ml is equivalent to 50 μg of the element and with the other 1 ml is equivalent to 5 μg of the element. Use these weaker solutions to prepare the standard oxides containing impurities below about the 0·2 per cent. level.

PREPARATION OF COMPOSITE SOLUTIONS—

Make all volumetric measurements as accurately as possible; use a burette.

Make up a series of individual composite solutions to simulate the composition of 0·5-g samples of the parent materials.

On a 0·5-g sample basis, prepare a series of composite solutions of copper, brass (80/20), brass (60/40), phosphor bronze (Cu 95, Sn 4·8 and P 0·2 per cent.), cupro-nickel (Cu 75 and Ni 25 per cent.), nickel-silver (Cu 60, Ni 15 and Zn 25 per cent.) and Everdur (Cu 96, Si 3 and Mn 1 per cent.).

PARENT SOLUTIONS—

These were composed as follows—

Material	Amount of solution/ml					
	A	B	C	D	E	J
Copper	10·0	—	—	—	—	—
Brass (80/20)	8·0	2·0	—	—	—	—
Brass (60/40)	6·0	4·0	—	—	—	—
Phosphor bronze	9·5*	—	—	—	—	2·0
Aluminium bronze ..	9·0	—	—	2·0	—	—
Cupro-nickel (75/25) ..	7·5	—	5·0	—	—	—
Nickel-silver	6·0	2·5	3·0	—	—	—
Everdur	9·6†	—	—	—	1·0	—

* Add 30·5 mg of finely divided high-purity tin(IV) oxide to these solutions.
† Add 15 mg of finely divided high-purity silica to these solutions.

IMPURITY ADDITIONS—

Impurity level, per cent.	0·5	0·3	0·2	0·1	0·05	0·01	0·005	0·001
Addition of solution/ml	5·0*	3·0*	2·0*	1·0*	5·0†	1·0†	5·0‡	1·0‡

* Containing 0·5 mg ml^{-1}.
† Containing 50 μg ml^{-1}.
‡ Containing 5 μg ml^{-1}.

For example, add 7·5 ml of solution A to 5·0 ml of solution C; this combined solution contains the same amount of copper and nickel as a 0·5-g sample of a nominal 75/25 cupro-nickel. Add 5·0 ml of each of the six 50 μg ml^{-1} solutions prepared by dilution of the F, G, H, I, J and K solutions.

This combined solution then contains, in addition to the parent metals, the same amounts of zinc, silver, bismuth, aluminium, manganese, iron, lead, arsenic, antimony, silicon, tin and phosphorus as those present in a 0·5-g sample of cupro-nickel containing 0·05 per cent. of these elements.

PREPARATION OF OXIDES—

Proceed with each composite solution as follows.

Evaporate the solution to dryness, then heat the residue to 400 °C for 15 minutes and cool it. Transfer the solid residue to a small agate pestle and mortar of the type that is an integral part of a Glen Creston mixing mill, and grind the oxide to a powder in the mill for about 2 minutes.

PREPARATION OF STANDARD OXIDE COMPARISON PLATE—

Transfer 0·3 g of each oxide powder, individually, to a standard graphite cup (height 9 mm, o.d. 12 mm, wall thickness 1 mm and base thickness 5 mm, *i.e.*, inside wall height 4 mm). and proceed with each as follows.

Tap the cup lightly several times to ensure uniform distribution of the powder. Place the cup on a graphite pillar (25 mm diameter), and examine spectrographically under the following conditions (expose each set of standards on a separate plate).

Spectrograph	Hilger and Watts Medium Quartz	Inductance	0·06 mH
		Sample polarity	Negative
Source unit	BNF General-purpose	Filter	7 step
Counter electrode	High-purity graphite rod (6 mm diameter), *e.g.*,	Source-to-slit distance	380 mm
		Gap	3 mm
	Ringsdorff RWO 90° cone	Pre-burn	Nil
Capacitance	250 μF	Exposure	15 s
Resistance	10 Ω	Plate	Ilford N40

Develop the plate for 2 minutes at 26 $\pm$ 0·5 °C by using diluted Johnson's Universal Developer (15 + 85). Rinse the plate, fix and wash it thoroughly, then dry it in a dust-free atmosphere.

PROCEDURE—

Transfer about 0·3 g of the sample to a 100-ml squat beaker, add 5 ml of dilute nitric acid (1 + 1), warm until the sample has dissolved, then evaporate the solution to dryness. Heat to 400 °C for 15 minutes, then transfer the solid residue to a small agate pestle and mortar of the type that is an integral part of a Glen Creston mixing mill. Grind the oxide to a powder in the mill for about 2 minutes, then proceed as in Preparation of Standard Oxide Comparison Plate. It is permissible to use a 2-step (0·66) filter and an exposure of 10 seconds.

EVALUATION OF SPECTRA—

Compare densities of the lines (Table I) in the sample spectrum with the standard spectra, and evaluate the concentrations of the impurity elements. To reduce the effect of possible interferences, compare three lines for each element whenever possible and record the lowest value. Care should be taken to ensure that spectra of comparable densities are used in this evaluation.

TABLE I

RECOMMENDED LINES FOR USE WITH PLATE-COMPARISON PROCEDURE

Element	Line, λ/nm	Element	Line, λ/nm
Tin	284·00	Silver	338·29
	286·33		241·32
	285·06		237·51
Lead	283·31	Antimony	231·15
	287·33		217·59
	282·32		259·81
Iron	248·81	Bismuth	306·77
	296·69		289·80
	297·32	Arsenic	234·98
Nickel	305·08		286·05
	313·41	Silicon	288·16
	308·08		251·61
Manganese	294·92		251·43
	288·96	Zinc	330·29
	423·53		334·50
Aluminium	396·15	Phosphorus	253·57
	394·40		255·33
	308·20		253·40

TABLE IIa: COMPARISON OF RESULTS (PER CENT.)

Sample	Material	Sn	Pb	Fe	Ni	Mn	Al
S281	Copper (D.O.)	*0·133*	*0·115*	*0·100*	*0·119*	*0·076*	*0·11*
		0·1–0·2	0·1–0·2	0·1–0·2	0·1–0·2	~0·1	~0·1
		0·1–0·2	~0·1	0·1–0·2	0·1–0·2	0·05–0·1	0·1–0·2
		~0·1	~0·1	0·1–0·2	0·1–0·2	~0·1	~0·1
S282		*0·044*	*0·041*	*0·029*	*0·041*	*0·015*	*0·009*
		~0·05	~0·05	~0·05	~0·05	0·01–0·05	~0·01
		~0·05	~0·05	0·01–0·05	~0·05	0·01–0·05	~0·01
		0·01–0·05	0·01–0·05	~0·05	0·01–0·05	~0·01	~0·01
S283		*0·011*	*0·0055*	*0·0014*	*0·013*	*<0·005*	*0·007*
		0·01–0·05	~0·01	0·001–0·005	~0·01	<0·001	~0·001
		0·01–0·05	0·005–0·01	0·001–0·005	0·01–0·05	<0·001	~0·001
		~0·01	0·005–0·01	~0·001	~0·01	<0·001	~0·001
S284		*0·003*	*0·0029*	*0·0008*	*0·005*	*<0·0005*	*0·003*
		0·001–0·005	0·001–0·005	~0·001	~0·005	<0·001	~0·001
		0·005	0·001–0·005	~0·001	~0·005	<0·001	~0·001
		0·001–0·005	0·001–0·005	~0·001	~0·005	<0·001	~0·001
S217	Brass (60/40)	*0·122*	*0·112*	*0·139*	*0·136*	*0·076*	*0·036*
		~0·1	~0·1	0·1–0·2	~0·1	~0·1	~0·05
		0·1–0·2	~0·1	0·1–0·2	0·1–0·2	~0·1	0·01–0·05
		~0·1	~0·1	0·1–0·2	~0·1	~0·1	~0·05
S218		*0·038*	*0·04*	*0·036*	*0·047*	*0·003*	*<0·002*
		~0·05	0·01–0·05	~0·05	0·01–0·05	0·001–0·005	<0·001
		~0·05	0·01–0·05	~0·05	~0·05	0·001–0·005	~0·001
		~0·05	0·01–0·05	0·01–0·05	~0·05	0·001–0·005	~0·001
S219		*0·0157*	*0·0135*	*0·014*	*0·0153*	*0·002*	—
		~0·01	~0·01	~0·01	~0·01	0·001–0·005	—
		0·01–0·05	~0·01	0·01–0·05	0·01–0·05	~0·001	—
		~0·01	0·01–0·05	0·01–0·05	~0·01	0·001–0·005	—
S220		*0·0037*	*0·005*	*0·002*	*0·006*	—	—
		~0·005	~0·005	—	~0·005	—	—
		0·001–0·005	~0·005	~0·005	—	—	—
		0·001–0·005	~0·005	~0·005	—	—	—
S277	85% Copper 15% Zinc	*0·144*	*0·122*	*0·102*	*0·120*	*0·077*	*0·073*
		~0·1	~0·1	~0·1	~0·1	~0·1	0·05–0·1
		0·1–0·2	0·1–0·2	0·1–0·2	0·1–0·2	0·05–0·1	0·05–0·1
		0·1–0·2	~0·1	0·1–0·2	0·1–0·2	0·05–0·1	0·05–0·1
S278		*0·045*	*0·044*	*0·038*	*0·040*	*0·024*	*0·025*
		~0·05	~0·05	~0·05	~0·05	0·01–0·05	0·01–0·05
		0·05–0·1	~0·05	~0·05	~0·05	0·01–0·05	0·01–0·05
		~0·05	~0·05	~0·05	~0·05	~0·05	~0·01
S279		*0·010*	*0·012*	*0·013*	*0·012*	*0·007*	*0·008*
		~0·01	~0·01	~0·01	~0·01	~0·005	0·005
		~0·01	~0·01	~0·01	~0·01	~0·005	0·005–0·01
		~0·01	~0·01	~0·01	~0·01	~0·005	0·005
S280		*0·003*	*0·0057*	*0·005*	*0·005*	*0·005*	*0·006*
		0·001–0·005	~0·005	~0·005	~0·005	0·001–0·005	~0·001
		0·001–0·005	0·001–0·005	~0·005	~0·005	~0·005	~0·001
		0·001–0·005	~0·005	0·001–0·005	0·001–0·005	~0·001	~0·001
S423	75% Copper 25% Nickel	*0·095*	*0·088*	*0·080*	—	*0·014*	*0·0015*
		~0·1	~0·1	~0·1	—	0·01–0·05	~0·001
		~0·1	~0·1	~0·1	—	0·01–0·05	~0·001
		~0·1	~0·1	~0·1	—	0·01–0·05	~0·001
S424		*0·030*	*0·033*	*0·025*	—	*<0·001*	*0·002*
		~0·05	~0·05	~0·05	—	~0·001	~0·001
		~0·05	~0·05	0·01–0·05	—	<0·001	~0·001
		0·05	0·05	0·01–0·05	—	<0·001	~0·001
S425		*0·012*	*0·015*	*0·020*	—	*0·001*	*0·002*
		0·01–0·05	0·01–0·05	0·01	—	~0·001	~0·001
		0·01	0·01–0·05	0·01	—	<0·001	~0·001
		0·01	0·01	0·01–0·05	—	<0·001	~0·001
S426		*0·0065*	*0·032*	*0·020*	—	*0·0015*	*0·002*
		~0·005	0·01–0·05	0·01–0·05	—	~0·001	~0·001
		0·001–0·005	~0·05	0·01–0·05	—	~0·001	~0·001
		~0·005	~0·05	~0·05	—	~0·001	~0·001

First row (italics): results by alternative methods. Second, third and fourth rows: independent results by

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Ag	Sb	Bi	As	Si	P	Zn	Sample
0·062	*0·01*	*0·012*	*0·113*	*0·064*	*0·133*	*0·158*	S281
∼0·05	∼0·01	∼0·01	0·1–0·2	0·05–0·1	∼0·1	0·1–0·2	
0·05–0·1	∼0·01	∼0·01	0·1–0·2	0·05–0·1	0·1–0·2	0·1–0·2	
∼0·05	0·01–0·05	∼0·01	0·1–0·2	∼0·1	∼0·1	∼0·1	
0·022	*0·003*	*0·004*	*0·038*	*0·008*	*0·058*	*0·055*	S282
∼0·01	∼0·005	0·001–0·005	∼0·05	∼0·01	∼0·05	0·05–0·1	
∼0·05	<0·005	0·001–0·005	∼0·05	0·005–0·01	∼0·05	0·05–0·1	
0·01–0·05	0·001–0·005	0·001–0·005	0·01–0·05	0·005–0·01	∼0·05	0·01–0·05	
0·008	*0·0008*	*0·001*	*0·013*	*0·005*	*0·019*	*0·0068*	S283
∼0·005	<0·005	∼0·001	0·01–0·05	<0·001	∼0·01	∼0·005	
∼0·01	<0·005	∼0·001	0·01–0·05	<0·001	∼0·01	0·01–0·05	
∼0·005	<0·005	∼0·001	0·01–0·05	<0·001	∼0·01	∼0·005	
0·003	*<0·0005*	*0·0005*	*0·0047*	*<0·005*	*0·023*	*0·0038*	S284
∼0·001	<0·005	<0·001	∼0·005	<0·001	0·01–0·05	<0·005	
0·001–0·005	<0·005	<0·001	∼0·005	<0·001	∼0·01	0·001–0·005	
0·001–0·005	<0·005	<0·001	∼0·005	<0·001	∼0·01	∼0·005	
0·043	*0·012*	*0·0096*	*0·116*	*0·061*	*0·125*	—	S217
0·01–0·05	∼0·01	∼0·01	∼0·1	0·05–0·1	∼0·1	—	
0·01–0·05	0·01–0·05	0·005–0·01	0·1–0·2	0·05–0·1	0·1–0·2	—	
0·01–0·05	0·01–0·05	∼0·01	∼0·1	0·05–0·1	0·1–0·2	—	
0·018	*0·004*	*0·0028*	*0·039*	*<0·001*	*0·024*	—	S218
0·01–0·05	∼0·005	0·001–0·005	∼0·05	<0·005	0·01–0·05	—	
0·01–0·05	<0·005	0·001–0·005	∼0·05	<0·001	0·01–0·05	—	
0·01–0·05	∼0·005	<0·005	∼0·05	∼0·001	∼0·01	—	
0·005	*0·0012*	*0·0012*	*0·013*	*0·0016*	*0·065*	—	S219
∼0·005	<0·005	∼0·001	∼0·01	<0·005	∼0·05	—	
0·005–0·01	<0·005	∼0·001	∼0·01	<0·001	∼0·05	—	
0·005–0·01	<0·005	∼0·001	∼0·01	<0·001	∼0·05	—	
—	*0·0003*	*0·0005*	*0·0042*	*<0·005*	*0·0004*	—	S220
—	<0·005	<0·001	<0·005	<0·005	<0·005	—	
—	<0·005	<0·001	<0·005	<0·001	<0·001	—	
—	<0·005	<0·001	<0·005	<0·001	<0·001	—	
0·061	*0·011*	*0·009*	*0·121*	*0·068*	*0·132*	—	S277
0·05–0·1	0·01–0·05	∼0·01	∼0·1	∼0·1	∼0·1	—	
∼0·1	0·01–0·05	0·005–0·01	0·1–0·2	∼0·1	0·1–0·2	—	
∼0·1	∼0·01	∼0·01	∼0·1	∼0·1	0·1–0·2	—	
0·022	*0·004*	*0·003*	*0·039*	*0·019*	*0·042*	—	S278
0·01–0·05	∼0·005	0·001–0·005	0·01–0·05	∼0·01	0·01–0·05	—	
∼0·05	0·001–0·005	0·001–0·005	∼0·05	∼0·01	∼0·05	—	
0·01–0·05	0·001–0·005	0·001–0·005	∼0·05	0·01–0·05	∼0·05	—	
0·007	*0·0009*	*0·0009*	*0·0114*	*0·005*	*0·013*	—	S279
0·005–0·01	<0·005	∼0·001	0·01–0·05	∼0·005	∼0·01	—	
∼0·005	<0·005	<0·001	0·005–0·01	0·001–0·005	∼0·01	—	
0·005–0·01	<0·005	∼0·001	0·005–0·01	0·001–0·005	∼0·01	—	
0·003	*0·0005*	*0·0004*	*0·004*	*<0·0005*	*0·004*	—	S280
∼0·005	<0·005	<0·001	∼0·005	<0·001	<0·005	—	
0·001–0·005	<0·005	<0·001	<0·005	<0·001	<0·005	—	
0·001–0·005	<0·005	<0·001	0·001–0·005	∼0·001	<0·005	—	
0·053	*0·0095*	*0·009*	*0·096*	*0·0025*	*0·088*	*0·11*	S423
0·05–0·1	∼0·01	∼0·01	0·1–0·2	∼0·005	0·05–0·1	∼0·1	
0·05–0·1	∼0·01	∼0·01	∼0·1	∼0·005	0·05–0·1	0·1–0·2	
∼0·05	∼0·01	∼0·01	∼0·1	∼0·005	∼0·1	0·05–0·1	
0·024	*0·003*	*0·003*	*0·031*	*0·0015*	*0·009*	*0·023*	S424
0·01–0·05	∼0·005	0·001–0·005	∼0·05	∼0·001	0·005–0·01	∼0·05	
0·01–0·05	∼0·005	0·001–0·005	∼0·05	∼0·001	∼0·01	∼0·05	
∼0·05	∼0·005	∼0·005	∼0·05	∼0·001	∼0·01	0·01–0·05	
0·012	*0·001*	*0·001*	*0·012*	*0·0015*	*0·003*	*0·015*	S425
0·01–0·05	∼0·001	0·001–0·005	0·005–0·01	∼0·001	0·001–0·005	∼0·01	
0·01–0·05	∼0·001	∼0·001	∼0·01	∼0·001	0·001–0·005	∼0·01	
0·01–0·05	∼0·001	∼0·001	∼0·01	∼0·001	<0·005	∼0·01	
0·004	*0·0015*	*0·0002*	*0·004*	*0·0010*	*0·003*	*0·21*	S426
∼0·005	∼0·001	<0·001	0·001–0·005	0·001–0·005	∼0·005	∼0·2	
∼0·005	∼0·001	<0·001	∼0·005	0·001–0·005	0·001–0·005	∼0·2	
∼0·005	∼0·001	<0·001	∼0·005	∼0·001	0·001–0·005	∼0·2	

recommended spectrographic method with three independent analysts.

RESULTS AND CONCLUSIONS

Adequate sensitivities were obtained, and line densities of the spectra showed a gradual increase with increase in impurity content at the wavelengths used. The blank in no instance exceeded 10 p.p.m. of the element to be determined.

When densities of the selected impurity lines for any of the seven materials were compared, all were in remarkably close agreement at all impurity levels. A possible explanation for this agreement is that all of the finely divided oxide entering the plasma is completely excited. This observation implies that the impurity-line intensities are independent of matrix composition, the significance of which is that a single calibration for all of the types of materials examined is adequate. It is, therefore, reasonable to speculate that other copper-base alloys would respond in the same way.

Typical standards of known composition are a prerequisite of most spectrographic analyses, and the recommended method of preparing oxides with known levels of impurities meets this requirement in the analysis of samples of small dimensions.

Results in Tables II*a*, II*b*, II*c* and III show the level of agreement obtained by the three analysts, who reported, independently, their visual interpretation of the same spectra, and also a comparison of their results with those obtained by alternative, often time-consuming, non-spectrographic procedures.

It is not recommended that small samples should be supplied for spectrographic analysis when massive samples can be made available, because the recommended method takes much longer than any established spectrographic procedure for analysing massive samples. The

TABLE II*b*

COMPARISON OF RESULTS (PER CENT.) FOR 95 PER CENT. COPPER, 4·8 PER CENT. TIN, 0·2 PER CENT. PHOSPHORUS ALLOYS

Sample	Zn	Pb	Fe	Ni	Bi	As	P
S135	*0·10*	—	—	—	—	—	—
	~0·1	—	—	—	—	—	—
	~0·1	—	—	—	—	—	—
	~0·1	—	—	—	—	—	—
S136	*0·006*	—	—	—	—	—	—
	~0·005	—	—	—	—	—	—
	~0·005	—	—	—	—	—	—
	~0·005	—	—	—	—	—	—
S137		*0·005*	—	—	*0·001*	—	—
	—	~0·005	—	—	~0·001	—	—
	—	~0·005	—	—	~0·001	—	—
	—	~0·005	—	—	~0·001	—	—
S138		*0·004*		—	*0·0013*	—	—
	—	~0·005	—	—	~0·001	—	—
	—	~0·005	—	—	~0·001	—	—
	—	0·001–0·005	—	—	~0·001	—	—
S139		*0·002*	—	—	*0·0008*	*<0·005*	*0·012*
	—	~0·001	—	—	<0·001	0·001–0·005	~0·01
	—	~0·001	—	—	<0·001	0·001–0·005	~0·01
	—	~0·001	—	—	<0·001	0·001–0·005	~0·01
S140		*0·005*	—	—	*0·0027*	*0·005*	*0·018*
	—	~0·005	—	—	0·001–0·005	0·001–0·005	0·01
	—	~0·005	—	—	0·001–0·005	0·001–0·005	0·01
	—	~0·005	—	—	0·001–0·005	0·001–0·005	0·01
S143		*0·06*	*0·01*	*0·02*		*0·015*	*0·14*
	—	~0·1	0·01–0·05	0·01–0·05	—	0·01–0·05	0·1–0·2
	—	0·05–0·1	0·01–0·05	0·01–0·05	—	0·01–0·05	0·1–0·2
	—	~0·05	~0·01	0·01–0·05	—	~0·01	0·1–0·2
S144							*0·18*
	—	—	—	—	—	—	0·1–0·2
	—	—	—	—	—	—	0·1–0·2
	—	—	—	—	—	—	0·1–0·2
S555							*0·05*
	—	—	—	—	—	—	0·05
	—	—	—	—	—	—	0·05
	—	—	—	—	—	—	0·05

recommended method does, however, enable samples of wire and thin sheet, and other samples of similar small dimensions, to be analysed spectrographically to meet the requirements made on the laboratory for the determination of specified impurity levels in certain grades of copper and in a range of copper-base materials.

It cannot be claimed that the method is as accurate as some alternative procedures but, provided its limitations are appreciated and the analytical results obtained are adequate, a wide range of impurity elements can be determined in a single sample within 90 minutes, and several samples can be analysed concurrently.

TABLE IIc

COMPARISON OF RESULTS (PER CENT.) FOR 76 PER CENT. COPPER, 22 PER CENT. ZINC, 2 PER CENT. ALUMINIUM ALLOYS

Sample	Sn	Pb	Fe	Ni	As	Si
S552	0·08				0·042	
	~0·1	—	—	—	~0·05	—
	~0·1	—	—	—	~0·05	—
	~0·1	—	—	—	~0·05	—
S553	0·13				0·042	
	0·1–0·2	—	—	—	~0·05	—
	0·1–0·2	—	—	—	~0·05	—
	0·1–0·2	—	—	—	~0·05	—
S554	0·18				0·044	
	0·1–0·2	—	—	—	~0·05	—
	0·1–0·2	—	—	—	~0·05	—
	~0·2	—	—	—	~0·05	—
S587		0·0095				
	—	~0·01	—	—	—	—
	—	~0·01	—	—	—	—
	—	~0·01	—	—	—	—
S588			0·019			
	—	—	0·01–0·05	—	—	—
	—	—	0·01–0·05	—	—	—
	—	—	0·01–0·05	—	—	—
S589					0·016	
	—	—	—	—	0·01–0·05	—
	—	—	—	—	0·01–0·05	—
	—	—	—	—	0·01–0·05	—
S590						0·004
	—	—	—	—	—	0·005
	—	—	—	—	—	0·005
	—	—	—	—	—	0·005
S591						0·007
	—	—	—	—	—	0·005–0·01
	—	—	—	—	—	0·005–0·01
	—	—	—	—	—	~0·01
S592	0·0045			0·07		
	~0·005	—	—	0·05–0·1	—	—
	~0·005	—	—	0·05–0·1	—	—
	~0·005	—	—	0·05–0·1	—	—
S593	0·018				0·044	
	0·01–0·05	—	—	—	0·01–0·05	—
	0·01–0·05	—	—	—	~0·05	—
	0·01–0·05	—	—	—	0·01–0·05	—
S594	0·038					
	~0·05	—	—	—	—	—
	0·01–0·05	—	—	—	—	—
	~0·05	—	—	—	—	—

TABLE III

ADDITIONAL RESULTS (PER CENT.)

Sample	Material	Added	Element			
				Found by		
			Alternative method	Recommended method		
S135	Phosphor bronze 95% Cu, 4·8% Sn, 0·2% P	Zinc	0·10	~0·1	~0·1	~0·1
S136		Zinc	0·006	~0·005	~0·005	~0·005
S137		Lead	0·005	~0·005	~0·005	~0·005
		Bismuth	0·001	~0·001	~0·001	~0·001
S138		Lead	0·004	~0·005	~0·005	~0·001-0·005
		Bismuth	0·0013	~0·001	~0·001	~0·001
S139		Lead	0·002	~0·001	~0·001	~0·001
		Bismuth	0·0008	<0·001	<0·001	<0·001
		Arsenic	<0·005	0·001-0·005	0·001-0·005	0·001-0·005
		Phosphorus	0·012	~0·01	~0·01	~0·01
S140		Lead	0·005	~0·005	~0·005	~0·005
		Bismuth	0·0027	0·001-0·005	0·001-0·005	0·001-0·005
		Arsenic	0·005	0·001-0·005	0·001-0·005	0·001-0·005
		Phosphorus	0·018	~0·01	~0·01	~0·01
S143		Lead	0·06	0·05-0·1	~0·1	~0·05
		Iron	0·01	0·01-0·05	0·01-0·05	~0·01
		Nickel	0·02	0·01-0·05	0·01-0·05	0·01-0·05
		Arsenic	0·015	0·01-0·05	0·01-0·05	~0·01
		Phosphorus	0·14	0·1-0·2	0·1-0·2	0·1-0·2
S144		Phosphorus	0·18	0·1-0·2	0·1-0·2	0·1-0·2
S555		Phosphorus	0·05	~0·05	~0·05	~0·05
S552	Alumbro 76% Cu, 22% Zn, 2% Al	Tin	0·08	~0·1	~0·1	~0·1
		Arsenic	0·042	~0·05	~0·05	~0·05
S553		Tin	0·13	0·1-0·2	0·1-0·2	0·1-0·2
		Arsenic	0·042	~0·05	~0·05	~0·05
S554		Tin	0·18	0·1-0·2	0·1-0·2	0·2
		Arsenic	0·044	~0·05	~0·05	~0·05
S587		Lead	0·0095	~0·01	~0·01	~0·01
S588		Iron	0·019	0·01-0·05	0·01-0·05	0·01-0·05
S589		Arsenic	0·016	0·01-0·05	0·01-0·05	0·01-0·05
S590		Silicon	0·004	~0·005	~0·005	~0·005
S591		Silicon	0·007	0·005-0·01	0·005-0·01	~0·01
S592		Tin	0·0045	~0·005	~0·005	~0·005
		Nickel	0·07	0·05-0·1	0·05-0·1	0·05-0·1
S593		Tin	0·018	0·01-0·05	0·01-0·05	0·01-0·05
		Arsenic	0·044	~0·05	0·01-0·05	0·01-0·05
S594		Tin	0·038	~0·05	~0·05	0·01-0·05

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