RI 7878

JLB

Bureau of Mines Report of Investigations/1974

Rapid Identification of Copper-Base Alloys by Energy Dispersion X-Ray Analysis

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 7878

Rapid Identification of Copper-Base Alloys by Energy Dispersion X-Ray Analysis

By Harold E. Marr III
College Park Metallurgy Research Center, College Park, Md.

MARCH 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
Rogers C. B. Morton, Secretary

BUREAU OF MINES
Thomas V. Falkie, Director

This publication has been cataloged as follows:

Marr, Harold E
Rapid identification of copper-base alloys by energy dispersion X-ray analysis. [Washington] U.S. Bureau of Mines [1974]

15 p. illus., tables. (U.S. Bureau of Mines. Report of investigations 7878)

Includes bibliography.

1. Copper alloys. 2. X-rays—Industrial applications. I. U.S. Bureau of Mines. II. Title. (Series)

TN23.U7 no. 7878 622.06173

U.S. Dept. of the Int. Library

CONTENTS

ILLUSTRATIONS

TABLES

RAPID IDENTIFICATION OF COPPER-BASE ALLOYS BY ENERGY DISPERSON X-RAY ANALYSIS

by

Harold E. Marr III[1]

ABSTRACT

Energy dispersion X-ray analysis was evaluated for possible application in the secondary metals industries for the rapid analysis and identification of copper-base alloys. Laboratory investigations of standard brass and bronze samples indicate that X-ray methods are capable of separating standard alloys into 10 general classes with analytical times of less than 3 seconds per sample for clean, flat samples. A radioactive source of americium 241 with a secondary fluorescer was used as an excitation source, and a lithium-drifted silicon semiconductor detector was utilized for energy discrimination of X-rays.

INTRODUCTION

Conservation of natural resources through recycling of secondary materials is a major objective of the Bureau of Mines metallurgy research program. One aspect of this program is to improve the efficiency of recycling scrap metals by the introduction of new technologies to the associated industries. Research on the rapid identification and sorting of nonferrous scrap metals has been in progress at the College Park Metallurgy Research Center for several years (4, 10).[2]

At present, in the routine operation of a commercial scrap yard, the degree of separation of the scrap metals depends on the abilities of experienced sorters to identify the alloys by object recognition or by means of a limited number of physical or chemical tests. The number of available skilled scrap sorters is decreasing, at the same time that the need for recycling is increasing, thereby forcing increased attention to the possibility of automation in the recycling industry.

The need for instrumentation capable of rapid, nondestructive identification of alloys has stimulated research on X-ray methods of analysis. Energy dispersive X-ray techniques are particularly attractive for rapid analysis

---

[1] Research chemist.

[2] Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

because of the capabilities for simultaneous multielement determination. A variety of radiation sources, detectors, and readout devices are now commercially available. The use of radioisotope sources with a semiconductor detector provides an attractive combination of source and detector suitable for the analysis of copper-base alloys. The procedures outlined in this report are designed to anticipate the use of energy dispersive X-ray analysis in an on-line sorting operation. Because it is a limited study in a laboratory, using delicate electronic instrumentation and a timesharing computer for data manipulation, only some of the questions are discussed that must be resolved in the development of a method for rapid identification of copper-base alloys in an industrial operation.

BACKGROUND

There are two major steps in the procedure for brass sorting, (1) the determination of the alloy composition and (2) the classification of the alloy by composition. The classification scheme is complicated by the fact that some copper-bearing materials cycled through scrap operations do not necessarily meet any well-defined and universally accepted set of specifications for composition.

The determination of composition of copper-base alloys by X-ray methods has already been well documented. Sophisticated calculations have been developed to correct for interelement effects in fluorescent X-ray analysis (1-3, 5, 7). These matrix corrections permit accurate determinations of the alloying constituents in carefully prepared samples that vary in composition over a limited range or where only two or three components are varied. The copper-bearing alloys cover a wide range of compositions, as indicated by the following percentages: copper 55-100, tin 0-10, lead 0-25, zinc 0-40, aluminum 0-12, nickel 0-26, iron 0-5, manganese 0-5, silicon 0-5. The use of portable X-ray instrumentation in a brass recycling operation has already been discussed (4, 11), but the best hope of completely automating a scrap operation seems to focus on energy dispersion X-ray analysis (6).

The copper-base alloys can be classified into more than 30 different brass and bronze alloys. For recycling, these are separated into about 5 to 15 groups depending on the degree of sorting required for the intended use. The requirements for precision and accuracy of the analysis are also determined by the intended use of the alloy. For example, if the analysis is to be used in the control of heats of metals in a foundry operation, a high degree of precision and accuracy is required. For this application, analytical times on the order of several minutes are acceptable. On the other hand, an analytical method that is rapid enough to be practical in a scrap sorting operation need only be precise enough to determine a sufficient number of components to distinguish the classes of alloys.

There are three steps in the procedure required to classify each piece of scrap: (1) the preparation of the sample, (2) the presentation of the sample to the detector, and (3) the measurement of some physical or chemical property. The most time-consuming step in the procedure will determine the rate of the sorting operation. Previously, step 3, the observation time, was presumed to be the slow step for X-ray analysis, because the sample must be observed long enough to collect a sufficient number of X-rays to correlate count rates to composition of the alloy. The purpose of this investigation was to determine if sufficient X-ray information for distinguishing groups of alloys could be acquired in short analytical times.

EXPERIMENTAL WORK

Determination of Composition of Copper-Base Alloys

Twenty-pound ingots of 23 brass and bronze alloys were purchased from a commercial source. The ingots were selected for compositions representative of the wide variety of copper-base alloys. A certificate of lot analysis was provided for each of the alloys, but no independent analyses of any ingots were made. Each ingot was sliced into 1/2-inch-thick sections, and the surface of a slice was turned down on a lathe.

A sealed radioisotope, americium 241, was selected as the excitation source. Americium 241 emits 60-keV gamma rays and 13.7- to 20.8-keV neptunium L X-rays. Direct excitation of the brass yielded a spectrum with a high background from incoherent scatter of the neptunium X-rays. The excitation efficiency of the 60-keV gamma radiation was relatively poor for copper, manganese, zinc, iron, and nickel, compared with tin. Therefore, filtering out the low-energy X-rays was not a satisfactory alternative, because the spectrum was dominated by the tin lines. In order to provide approximately the same excitation efficiency for all the elements of interest, a source-target assembly was selected as being the most effective means of excitation.

As shown in figure 1, the annular source of americium 241 (100 millicuries) was directed at the secondary fluorescer, which, in turn, was used to excite the sample. The secondary molybdenum K-radiation was effective for exciting the K-lines of copper, nickel, iron, zinc, and manganese, and the L-lines of lead; but the scattered 60-keV gamma rays from americium 241 were not sufficiently intense to excite enough tin K-radiation. Therefore a thin layer of barium carbonate was evenly deposited on the molybdenum foil target. The amount of barium carbonate was adjusted to be that which would yield approximately the same sensitivity for tin as for the other elements. One hundred milligrams of barium carbonate, mixed in a suspension of ethyl acetate, were deposited over an area of approximately 15 cm^2. The relative count for the elements in copper alloys from the dual target assembly is presented in table 1.

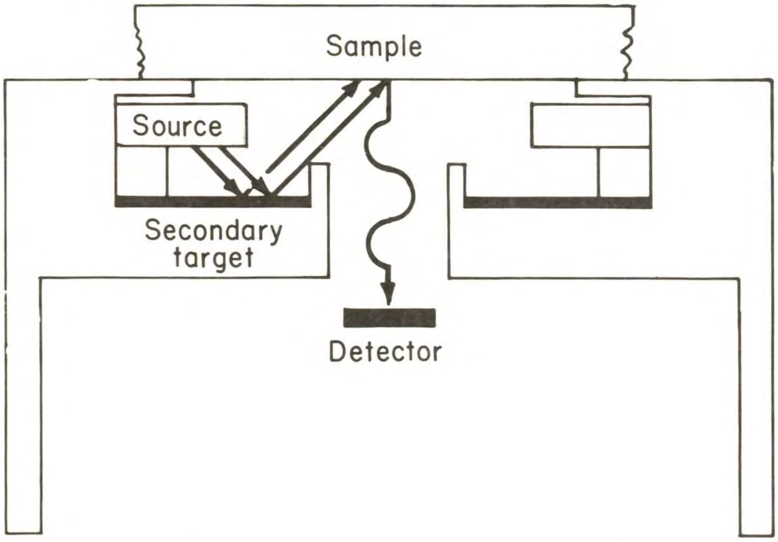

FIGURE 1. - Source-target assembly.

TABLE 1. - Relative count rate per percent alloying element in brass using molybdenum-barium excitation

	Cps/pct
Manganese, Kα	7
Iron, Kα	11
Nickel, Kα	9
Copper, Kα	10
Zinc, Kα	13
Lead, Lα	3
Tin, Kα	16

To illustrate the resolution of the X-ray lines using the semiconductor detector, a composite spectrum of two copper alloys is shown in figure 2. One alloy contained copper, zinc, lead, and tin; the other contained copper, iron, nickel, manganese, and aluminum. The determination of aluminum or silicon was not investigated in these studies, because the low energy of the characteristic X-rays would have made reliable analysis exceptionally difficult under the adverse conditions expected in an industrial sorting environment. The X-ray lines of molybdenum shown near the middle of the spectrum originate from a molybdenum foil used to shield the source holder. These lines do not interfere with the interpretation of the data.

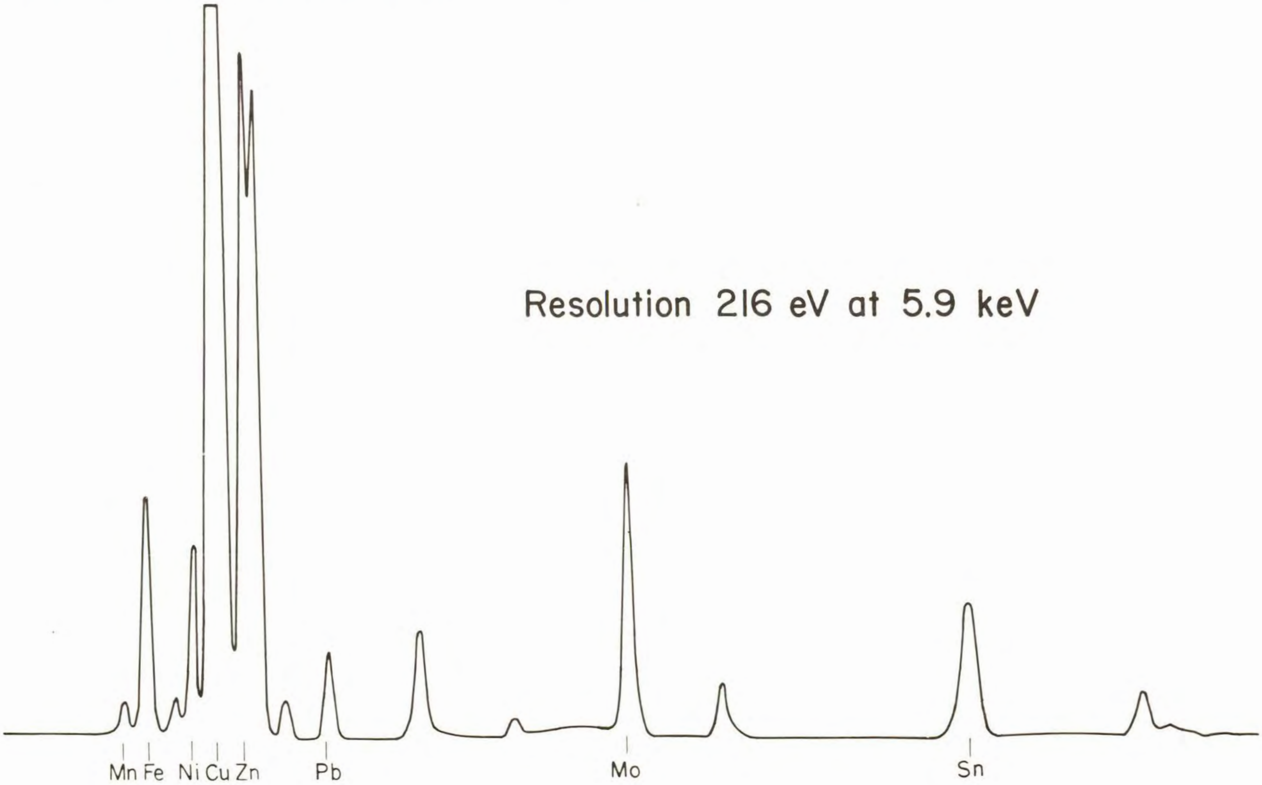

FIGURE 2. - Copper alloy spectrum.

The multichannel analyzer was set to include the energy range from 3 to 30 keV, a region that includes the X-ray lines of all the elements of interest. The lithium-drifted silicon semiconductor detector and associated electronics were calibrated with radioactive sources of iron 55 and cadmium 109 as well as with metal foils excited by americium 241. The counts were accumulated from the brass samples for a period of 10 minutes each in order to minimize the random errors due to counting statistics. The initial 10-minute runs were used to establish calibration curves and to compare the data with the results from a conventional X-ray spectrograph (4).

The 400-channel spectra from the calibration sources were processed through a computer program designed to smooth the spectra and locate the peaks (8). All the data reduction was accomplished by means of telephone-coupled communication with a timesharing computer facility (9). In an automated sorting operation, a dedicated computer would be used both as the multichannel analyzer and for the computations.

The intensities, after correction for background and overlap from $K\beta$ X-ray lines, were correlated to concentrations of the alloying elements by a linear least squares fit. No interelement corrections were applied initially, with the result that the copper intensity data yielded a standard deviation from the calibration curve that corresponded to 4-1/2 weight-percent copper.

As expected, determinations of samples with high lead or tin content had lower values than comparable determinations in alloys with low levels of heavy metals. Observation of the calibration curve of copper indicated that the determinations of copper were about 10 percent low in samples that contained 10 percent tin, suggesting that if the tin content were known, a simple matrix correction could be applied to intensities of the other lines to bring these values closer to the calibration curves. New calibration curves were established using a matrix correction, and the calculated concentrations were compared to the lot analyses. In this situation the order of the sequential determinations becomes important. The order of analysis was selected to be lead, tin, manganese, iron, nickel, copper, and zinc. The lead was determined first and no interelement corrections were made. The tin concentration was next determined and adjusted in each sample by a factor depending on the previously determined lead content. The other determinations were corrected for the presence of tin and lead. The factors for all the determinations are listed in table 2.

TABLE 2. - Correction factors for interelement effects

Corrected intensity	= Observed intensity × factor
Lead	$f_1 = 1$
Tin	$f_2 = f_1 + 0.005 \times \text{pct Pb}$
Manganese	$f_3 = f_2 + 0.01 \times \text{pct Sn}$
Iron	$f_4 = f_3$
Nickel	$f_5 = f_4 + 0.01 \times \text{pct Mn} + 0.01 \times \text{pct Fe}$
Copper	$f_6 = f_5$
Zinc	$f_7 = f_6 + 0.01 \times \text{pct Ni}$

Except for the corrections for tin and lead content, the determinations are adjusted only for the effects of those elements whose K-absorption edges occur at a lower energy than the X-ray emission energy of the element being determined. The flow diagram in figure 3 illustrates how the sequence of determinations proceeds from the measured intensities of each of the X-ray lines to the calculated compositions of each alloy. Except for the value for lead, the coefficient 0.01 was chosen for each of the correction factors because these values were the order of magnitude of the corrections as determined by an empirical fit of the data. The low levels of iron, nickel, and manganese in the standards and the uncertainty in the analyses would not support the derivation of more precise correction factors using these elements. The corrections, as applied to copper and zinc determinations, are similar to those determined by Jenkens (7). These corrections reduced the error in analysis sufficiently for sorting applications.

An example of a brass analysis is given in table 3. The alloys that have high concentrations of lead and tin showed improvement in the analytical determination with the matrix corrections. Calculation 1 contains no interelement corrections, and calculation 2 includes the correction factors listed in table 2. The standard deviations from the calibration curves are listed as estimates of the error for each determination. The values are not specific

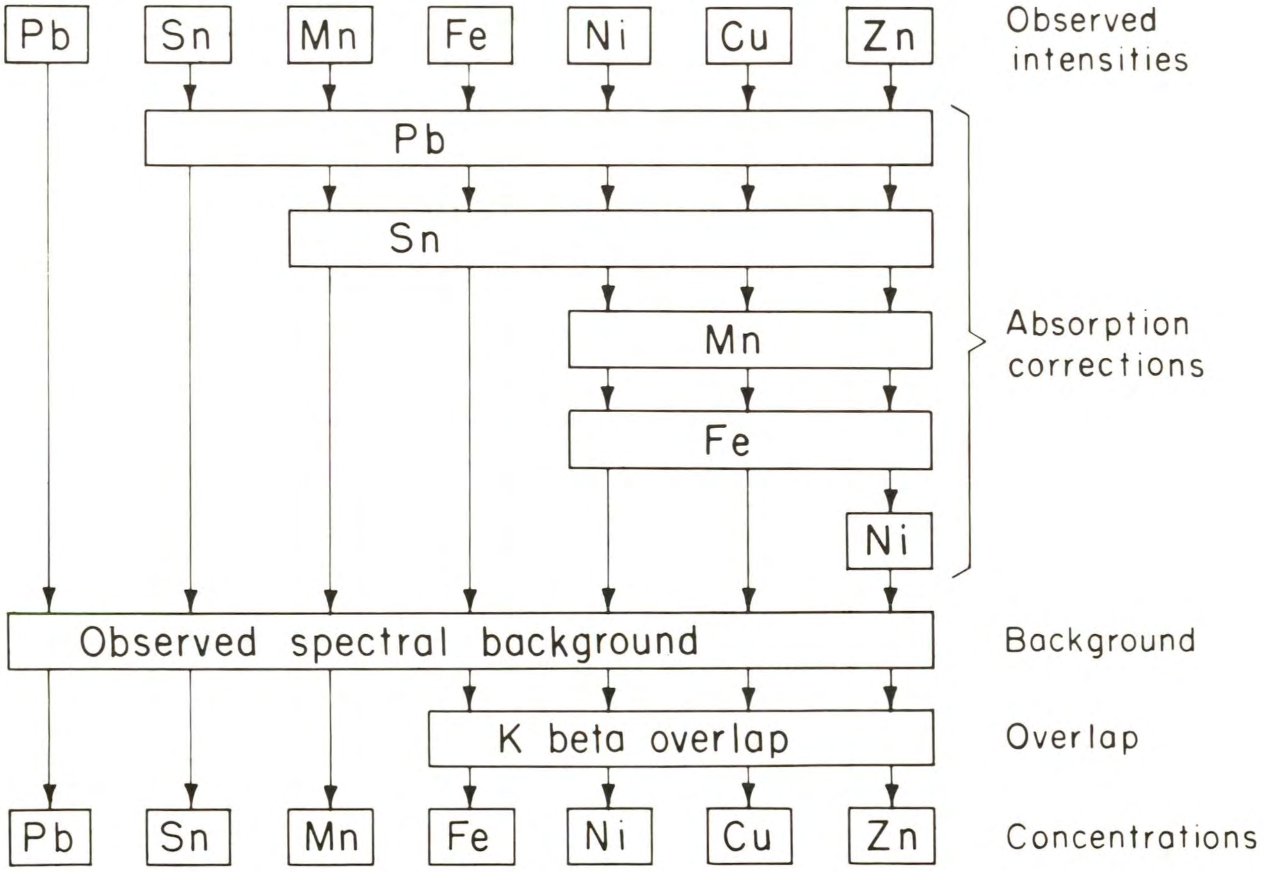

FIGURE 3. - Flow chart for X-ray calculations.

to this determination, but are the values determined for the entire set of data and are listed here for convenience. These standard deviations indicate that the average error in the determination of copper is approximately 4-1/2 weight-percent with no matrix correction and about 2-1/2 weight-percent when the correction is applied.

TABLE 3. - Analysis of red brass samples, weight-percent

(Semired, 76 metal--76-2.5-6.5-15)

Sample	Nominal lot analysis	No matrix correction	Matrix correction
Copper...........	75.04	74.74±4.66	75.36±2.50
Tin..............	2.79	2.74± .17	2.79± .01
Lead.............	7.53	7.61±1.11	7.61±1.11
Zinc.............	14.01	13.11± .50	13.61± .48
Iron.............	.20	.18± .08	.19± .08
Nickel...........	.37	.39± .06	.40± .06
Manganese........	-	.01± .02	.01± .02

In general, the reliability of an X-ray analytical method depends on how closely the standards match the unknown samples. Energy dispersion X-ray analysis is no exception, and for applications where a narrow range of compositions will be encountered, much better accuracy can be expected than for applications where wide ranges of composition are possible. This improvement in analysis can be dramatically illustrated by comparing the calculated values of copper content from several samples using three types of calibration curves, all of which correlate the same raw intensity data to concentration. Column 2 in table 4 shows the determination of copper using the calibration curve derived from the full set of 23 alloys. No interelement corrections were applied, and the standard deviation was 4.66 weight-percent. Column 3 gives the calculation concentrations from the calibration curves from the full set of data with matrix corrections applied and a standard deviation of 2.50 weight-percent. A calibration curve from six samples of tin bronze and red brass with narrow ranges of composition yielded the copper content in column 4. The matrix correction described earlier was applied to this limited set of data which had a standard deviation of 0.79 from the least squares fit of a line, demonstrating the improvement in the determinations when the composition varies only within narrow ranges. These values for the standard deviations from the calibration curves are significant in developing a method for sorting alloys, because they permit a comparison of the estimates of error expected for the several analytical procedures.

When the full set of data is used to construct the calibration curve, as would be necessary for some sorting applications, the major contributions to the larger standard deviations for copper, lead, and zinc are from the alloys with high lead or zinc content, as expected. For the purposes of rapid identification of alloys, a more critical determination is to establish the concentrations of minor elements, because the most stringent specifications are often concerned with the determination of low levels of these elements. Table 5 shows the values of the average errors for those determinations containing less than 1/2 percent of an element, indicating that good precision and accuracy can be attained where it is often most important.

TABLE 4. - Determination of copper, weight-percent

	(1) Nominal lot analysis	(2) No matrix correction, 23 samples	(3) Matrix correction, 23 samples	(4) Matrix correction, 6 samples
Red brass 85-5-5-5	84.46	82.49	83.40	84.80
Red brass 83-4-6-7	82.84	82.20	82.62	84.02
81 metal 81-3-7-9	79.25	78.39	78.70	78.86
76 metal 76-2.5-6.5-15	75.04	74.74	75.36	74.80
Gun metal 88-10-0-2	87.52	81.53	84.71	87.78
Navy G 88-8-0-4	87.22	82.68	84.68	86.08

TABLE 5. - Determination of errors in samples containing less than 1/2 percent of an element

Element	Number of determinations of less than 1/2 pct	Average error, wt-pct	Average, wt-pct
Tin.............	10	0.006	0.02
Lead............	11	.04	.03
Zinc............	6	.13	.07
Iron............	15	.03	.11
Nickel..........	19	.04	.12
Manganese.......	18	.02	.02

Sorting Copper-Base Alloys by Composition

From the preceding discussion, it is apparent that satisfactory analyses of copper-base alloys can be achieved by energy dispersive techniques. To evaluate the possible application of energy dispersion X-ray analysis to sorting scrap brass and bronze alloys, two restrictions were considered. The first problem is that only limited analytical times (less than 10 seconds per sample) are useful. Second, practical constraints are placed on the allowable errors in analysis, in terms of rigid specifications of composition which may be imposed, depending on the anticipated use of the sorted scrap. One such set of specifications for classification of alloys has been established by the Brass & Bronze Ingot Institute (BBII), as shown in table 6. For some applications, separation into a few broad categories may be sufficient; for other applications, a greater number of classifications may be necessary. In general, for any particular analytical scheme, the more rigid are the compositional specifications, the greater the sophistication of the equipment required, the higher the cost, and the longer the analytical time needed.

TABLE 6. - Chemical specifications for BBII standard alloys

Nominal Composition	Classification	Alloy Number	Copper, per cent			Tin, per cent			Lead, per cent			Zinc, per cent			Iron per cent			Aluminum per cent			Nickel per cent			Mang. per cent		Other Elements, maximum, per cent					
			Minimum	Nominal	Maximum	Minimum	Nominal	Maximum	Minimum	Nominal	Maximum	Minimum	Nominal	Maximum	Minimum	Nominal	Maximum	Minimum	Nominal	Maximum	Minimum	Nominal	Maximum	Minimum	Maximum	Antimony	Sulphur	Silicon	Phosphorus	Total named elements	Copper + Tin + Lead + Nickel, Min.
88-10-0-2	Tin Bronze	1A	86.0	88.0	89.0	9.5	10.0	10.5			0.25	1.5	2.0	3.0			0.15			none[b]			0.8[a]			0.25	0.05	0.005	0.03		
88-8-0-4	Tin Bronze	1B	86.0	88.0	89.0	7.8	8.0	9.0			0.25	3.5	4.0	5.0			0.20			none[b]			0.8[a]			0.25	0.05	0.005	0.03		
88-6-1½-4½	Leaded Tin Bronze	2A	86.0	88.0	89.0	5.8	6.0	6.5	1.0	1.5	1.8	3.5	4.0	5.0			0.20			none[b]			0.8[a]			0.20	0.05	0.005	0.03		
87-8-1-4		2B	85.0	87.0	89.0	7.8	8.0	9.0			0.9	3.0	4.0	5.0			0.20			none[b]			0.8[a]			0.25	0.05	0.005	0.03		
87-10-1-2		2C	86.0	87.0	88.5	9.3	10.0	10.5	0.8	1.0	1.3	1.3	2.0	2.5			0.15			none[b]			0.8[a]			0.25	0.05	0.005	0.03		
80-10-10	High Lead Tin Bronze	3A	78.0[c]	80.0	81.0	9.3	10.0	10.7	8.3	10.0	10.7			0.8			0.10			none[b]			0.8[a]			0.50	0.08	0.005	0.05		98.5
83-7-7-3		3B	82.0[c]	83.0	84.0	6.5	7.0	7.5	6.5	7.0	7.7	2.5	3.0	4.0			0.20			none[b]			0.8[a]			0.30	0.08	0.005	0.03		
85-5-9-1		3C	83.0[c]	85.0	85.0	4.5	5.0	5.5	8.5	9.0	9.7	0.5	1.0	1.5			0.10			none[b]			0.8[a]			0.35	0.08	0.005	0.04		98.0
78-7-15		3D	76.0[c]	78.0	79.0	6.0	7.0	7.5	14.0	15.0	16.0			0.8			0.10			none[b]			0.8[a]			0.50	0.08	0.005	0.05		98.5
70-5-25		3E	69.0	71.0	73.0	4.5	5.0	5.5	22.0	24.0	24.5			0.50			0.10			none[b]			0.8			0.8	0.08	0.005	0.05		98.5
85-5-5-5	Leaded Red Brass	4A	84.0[c]	85.0	86.0	4.3	5.0	6.0	4.0	5.0	5.7	4.5	5.0	6.0			0.25			none[b]			0.8[a]			0.25	0.08	0.005	0.03		
83-4-6-7		4B	82.0[c]	83.0	83.5	3.5	4.0	4.2	5.8	6.0	6.8	5.5	7.0	8.0			0.25			none[b]			0.8[a]			0.25	0.08	0.005	0.02		
81-3-7-9	Leaded Semi Red Brass	5A	79.0[c]	81.0	82.0	2.5	3.0	3.5	6.3	7.0	7.7	7.0	9.0	10.0			0.35			none[b]			0.8[a]			0.25	0.08	0.005	0.02		
76-2½-6½-15		5B	75.0[c]	76.0	76.7	2.3	2.5	3.0	6.0	6.5	7.0	13.0	15.0	16.0			0.35			none[b]			0.8[a]			0.25	0.08	0.005	0.01		
72-1-3-24	Leaded Yellow Brass	6A	70.0	72.0	73.0	0.7	1.0	1.7	1.5	3.0	3.5		remainder				0.50			none[b]			0.8			0.20	0.05	0.05	0.01		
67-1-3-29		6B	66.0	67.0	69.0		1.0	1.5	1.5	3.0	3.5		remainder				0.50			none[b]			0.8					0.05			
61-1-1-37		6C	58.0	61.0	63.0	0.5	1.0	1.5	0.8	1.0	1.5		remainder				0.50	0.0		0.50			0.8					0.05			
Mang. Bronze (60,000-15)	Leaded High Strength Yellow Brass (Mang. Bronze)	7A	56.0		62.0	0.5		1.0	0.5		1.3		remainder		0.8		1.5	0.25		1.0			0.8	0.10	0.50					note[2]	
Mang. Bronze (65,000-20)	High Strength Yellow Brass Manganese Bronze	8A	55.0		60.0			1.0			0.30		remainder		0.40		2.0	0.50		1.5			0.8		1.5					note[3]	
Mang. Bronze (90,000-18)		8B	60.0		68.0			0.10			0.10		remainder		2.0		4.0	3.0		7.5			0.8	2.5	5.0					note[6]	
Mang. Bronze (110,000-12)		8C	60.0		68.0			0.10			0.10		remainder		2.0		4.0	3.0		7.5			0.8	2.5	5.0					note[4]	
88-3-9	Aluminum Bronze	9A	86.0	88.0											2.5	3.0	4.0	8.5	9.0	9.5										99.0	
89-1-10		9B	86.0	89.0											0.8	1.0	1.5	9.0	10.0	11.0										99.0	
85-4-11		9C	83.0	85.0											3.0	4.0	5.0	10.0	11.0	11.5			2.5		0.5					99.5	
81-4-11-4		9D	78.0	81.0											3.0	4.0	5.0	10.0	11.0	11.5	3.0	4.0	5.5		3.5					99.5	
57-2-9-20-12	Leaded Nickel Brass (Nickel Silver)	10A	53.0	57.0	58.0	1.5	2.0	3.0	8.0	9.0	11.0		remainder				1.0			none[b]	11.0	12.0	14.0		0.50	0.35	0.08	Silicon Min. Max. 0.05	0.05		
60-3-5-16-16		10B	58.0	60.0	61.0	2.5	3.0	3.5	4.5	5.0	5.5		remainder				1.0			none[b]	15.5	16.0	17.0		0.50	0.25	0.08	0.05	0.05		
64-4-4-8-20	Leaded Nickel Bronze (Nickel Silver)	11A	63.0	64.0	65.0	3.5	4.0	4.5	3.5	4.0	5.0		remainder				1.0			none[b]	19.5	20.0	21.0		1.0	0.25	0.08	0.05	0.05		
66½-5-1½-2-25		11B	64.0	66.5	67.0	4.5	5.0	5.5	1.0	1.5	2.0		remainder				1.0			none[b]	24.0	25.0	26.0		1.0	0.20	0.08	0.05	0.05		
	Silicon Bronze	12A		remainder				1.0			0.5			5.0			2.5			1.5					1.5			1.0 5.0		99.5	
81-4-15	Silicon Brass	13B		remainder							0.5	12.0		16.0						0.5								3.0 5.0		99.5	

---

[a] By agreement between the manufacturer and the purchaser, a definite nickel content up to 0.80 per cent may be specified. In such a case, the nickel shall be within plus or minus 0.20 per cent of the desired content, and an analysis shall be made for it.

[b] The term "none" as applied to aluminum allowance is defined as 0.005 per cent determined on a 10-g. sample.

[c] In determining copper, minimum copper may be computed as copper plus nickel.

[2] Minimum Tensile Strength 60,000 lbs. Minimum Elongation in 2" 15%.

[3] Minimum Tensile Strength 65,000 lbs. Minimum Elongation in 2" 20%.

[4] Minimum Tensile Strength 110,000 lbs. Minimum Elongation in 2" 12%.

[5] Copper, Tin, Lead, Zinc, Nickel and Manganese must total 99.00%.

[6] Minimum Tensile Strength 90,000 lbs. Minimum Elongation in 2" 18%.

Two requirements for developing a computer-controlled sorting system are that some numerical value has to be assigned to each alloy which can be used by the computer to distinguish one alloy from another, and some means has to be devised to evaluate the reliability of each measurement. The appendix contains a discussion of the determination of error in X-ray analyses and a suggested method for comparing X-ray determinations of a given sample with a set of alloy specifications. Application of these methods to the 23 brass samples suggests that it is not difficult to design a separation scheme based on the nominal compositions of copper alloys, but it is important to include the possible measurement errors inherent in any real application. In practice, the specifications of copper alloys allow a tolerance about the nominal values, and therefore the sorting scheme may also take these tolerances into consideration. The 31 alloys listed in table 6 were compared for possible overlap of specifications when measurement error is taken into account and when elements like aluminum and silicon are not used in the separation scheme. For example, a copper alloy containing 83±2 percent copper, 4.2±0.2 percent tin, 5.9±0.3 percent lead, and 5.8±0.3 percent zinc might be identified as either 4A or 4B. Table 7 illustrates the decreased specificity in separating alloys as the measurement time is decreased from 60 seconds to 3 seconds of X-ray exposure.

TABLE 7. - Copper-base alloy separations that are achievable in 60 seconds and 3 seconds

Classification	BBII alloys	Classification	BBII alloys
		60 SECONDS	
1. Gun metal	1A	13. 60-65000 manganese bronze.	7A, 8A
2. Navy G	1B, 2B		
3. Leaded gun metal	2C	14. 90-110000 manganese bronze.	8C, 8B
4. Leaded tin bronze	2A		
5. High-lead tin bronze	3A	15. High-lead nickel brass.	10A
6. High-lead bronze	3E	16. Nickel brass	10B
7. Plastic bronze	3D	17. High-lead nickel bronze	11A
8. Bearing bronze 2	3C	18. Nickel bronze	11B
9. Bearing bronze 1	3B	19. Silicon brass	13B
10. Leaded red brass	4A, 4B, 5A	20. Si or Al bronze	12A, 9A, 9B, 9C
11. Semired brass	5B	21. Nickel aluminum bronze.	9D
12. Leaded yellow brass	6A, 6B, 6C		
		3 SECONDS	
1. Gun metal	1A, 1B, 2B, 2C	8. Yellow brass	6A, 6B, 6C, 7A, 8A, 8B, 8C
2. Leaded tin bronze	2A		
3. High-lead tin bronze	3A	9. Nickel silver	10A, 10B, 11A, 11B
4. Plastic bronze	3D, 3E		
5. Bearing bronze	3C, 3B	10. Si or Al alloy	12A, 13B, 9A, 9B, 9C, 9D
6. Red brass	4A, 4B, 5A		
7. Semired brass	5B		

Separation into 21 distinct categories is possible for exposure time of 60 seconds. This kind of sorting is beyond practical application. The problems of surface roughness and cleanliness of the samples overshadow the ability of a sorting scheme to distinguish between clean, flat alloys to this extent.

More practically, a separation into 10 groups with no overlap of specifications can be achieved in 3 seconds of X-ray exposure using energy dispersive X-ray analysis. Table 7 illustrates, for example, that an alloy in the composition range of 1A in the BBII specifications could be distinguished from all the other sets of BBII specifications in 60 seconds of X-ray analysis, and therefore be assigned to the narrow classification of "gun metal." In 3 seconds of X-ray analysis, the same alloy could not be uniquely distinguished from alloys 1B, 2B, and 2C, all of which are grouped under the broader classification "gunmetal." In the 3-second categories, "gunmetal," "Navy G," and "leaded gunmetal" are all collected under one broad classification.

DISCUSSION

A relatively weak source of radiation was used in this demonstration. It is more generally the capability of the detector to resolve X-ray energies at high count rate that is the limiting factor in determining the requirements of exposure time, although modern semiconductor detectors are capable of processing count rates of 20,000 counts per second without unacceptable loss of resolution. The fact that the data presented in this report were collected at X-ray counting rates of less than 2,000 counts per second would indicate that analytical times of less than 1 second are possible with X-ray systems that are already commercially available. The analytical time of 3 seconds was limited in this experiment by the strength of the radioisotopic source, not by the capabilities of the semiconductor detector. Therefore, by increasing the source strength or by using X-ray tubes with secondary targets, analytical times of less than a second would be feasible. Computation times in a dedicated computer are negligible.

Practical application of energy dispersion X-ray analysis in a scrap yard is not restricted by the availability of X-ray instrumentation. Sufficient information for many sorting tasks can be acquired in a few seconds of X-ray exposure times. Application is restricted by the engineering requirements for sample presentation. In general, scrap brass is not clean, nor is it flat, nor will it conveniently fit inside an X-ray machine.

Two of the sources of error in X-ray analysis are statistical counting errors and surface preparation. If the sample is ideal, then the counting error may predominate; if the accumulation time is long enough, the sample preparation may be the largest source of error. The sample surface problems may therefore contribute a different proportion of the error for different exposure times. The question is, how much can the cumulative error be in brass analysis and still be part of a useful method for sorting scrap? Presumably some type of X-ray device would be used on-line in an automated operation, and sand blasting or burnishing on a grinding wheel might be a possible means of exposing a clean surface. Part of the problem of irregularities in geometry can be alleviated by normalization of the total fluorescence count rate, by monitoring the total backscatter, or by other spectroscopic techniques. These problems are not insurmountable, but each sorting application is going to have to be carefully defined, in terms of how many separations are required, what analytical times are allowable, what technical competence is available, and how much the system will cost. Each of these questions will have to be considered in determining the feasibility of an energy dispersive X-ray system for application as a scrap-sorting device.

REFERENCES

1. Bäckerud, L. An Evaluation of the Suitability of X-ray Fluorescence Spectroscopy in the Analysis of Complex Alloy Systems. X-ray Spectrometry, v. 1, 1972, pp. 3-14.

2. _____. Determination of Copper in Complex Brasses by X-Ray Fluorescence Spectroscopy. Applied Spectroscopy, v. 21, No. 5, 1967, pp. 315-324.

3. Bareham, F. R., and J. G. M. Fox. X-Ray Fluorescence Analysis and Its Application to Copper Alloys. J. Inst. Metals, v. 88, 1959-60, pp pp. 344-351.

4. Campbell, W. J., and H. E. Marr III. Identification and Analyses of Copper-Base Alloys by Fluorescent X-Ray Spectrography. BuMines RI 7635, 1972, 30 pp.

5. Gidley, J. A. F. X-Ray Fluorescence Analysis of Copper Alloys. Ch. 1 in Spectroscopy in the Metallurgical Industry, Papers, 2d Buxton Symp., Derbyshire, England, July 1962. 1963, pp. 3-11.

6. Harrison, P. E., and B. T. Kenna. Qualitative Identification of Alloys by Energy-Dispersive X-Ray Spectroscopy. Talanta, v. 19, 1972, pp. 810-814.

7. Jenkens, R. Analysis of Copper-Base Alloys by X-Ray Fluorescence Spectroscopy. Norelco Reporter, v. 15, 1968, pp. 6-10, 29.

8. Marr III, H. E. Mathematical Smoothing of Digitized X-Ray Spectra. BuMines IC 8553, 1972, 15 pp.

9. Marr III, H. E., and W. J. Campbell. The Processing of Energy Dispersion X-Ray Data on a Timesharing Computer. Advances in X-Ray Analysis, v. 16, 1973, pp. 206-216.

10. Maynard, A. W., and H. S. Caldwell, Jr. Identification and Sorting of Nonferrous Scrap Metals. Proc. 3d Mineral Waste Utilization Symp., Chicago, Ill., Mar. 14-16, 1972. ITT Research Institute, Chicago, Ill., 1972, pp. 255-264.

11. Sellers, B., and J. Brinkerhoff. Signature Comparison Technique for Rapid Alloy Sorting With a Radioisotope Excited X-Ray Analyzer. Materials Research and Standards, v. 10, November 1970, pp. 16-18.

APPENDIX

Determination of Error

In X-ray methods of analysis, the error of each independent determination has two contributing terms, a systematic error arising from the particular analytical procedure (interelement effects, calibration, sample preparation) and a time-dependent error based on the statistics of the counting of X-rays. The random error in any given measurement can be calculated for any specified accumulated count once the error is determined for another known accumulated count. Table A-1 indicates the errors expected in the X-ray determinations of seven elements in brass and bronze alloys for several analytical times, at three levels of weight-percent concentrations. The error is calculated from the following equation:

$$\text{Error} = E_1 + \frac{3}{MT}\sqrt{I}, \qquad \text{(A-1)}$$

where E_1 is a time-independent error derived from the standard deviations from the original calibration curves determined by the 23 measured brass and bronze alloys. The second term is a function of the intensity collected and therefore is time dependent. T = time, M = slope of calibration curve, and $\sqrt{I}$ is the standard deviation from I counts.

TABLE A-1. - Errors expected in the energy dispersive analysis of brass alloys

Time, sec	Errors by indicated element concentration			Time, sec	Errors by indicated element concentration		
Copper...	55 pct	70 pct	90 pct	Manganese	0 pct	0.5 pct	3 pct
600	2.48	2.52	2.56	600	0.04	0.06	0.10
60	3.09	3.21	3.46	60	.11	.15	.29
10	4.39	4.67	5.00	10	.24	.36	.68
5	5.30	5.70	6.16	5	.33	.50	.96
1	9.15	10.03	11.07	1	.73	1.09	2.12
Lead.....	0 pct	5 pct	15 pct	Iron.....	0 pct	0.5 pct	3 pct
600	0.07	0.20	0.32	600	0.05	0.06	0.10
60	.14	.57	.95	60	.11	.14	.25
10	.28	1.35	2.28	10	.23	.32	.57
5	.38	1.89	3.21	5	.31	.44	.80
1	.82	4.18	7.12	1	.67	.94	1.75
Tin......	0 pct	2 pct	10 pct	Nickel...	0 pct	5 pct	25 pct
600	0.01	0.05	0.10	600	0.07	0.13	0.24
60	.03	.14	.31	60	.14	.34	.69
10	.06	.34	.75	10	.30	.79	1.64
5	.08	.48	1.06	5	.41	1.10	2.30
1	.19	1.07	2.37	1	.87	2.42	5.10
Zinc.....	0 pct	10 pct	40 pct				
600	0.15	0.23	0.34				
60	.20	.47	.80				
10	.30	.97	1.78				
5	.37	1.32	2.47				
1	.68	2.79	5.37				

Probabilities for Identification

In an automated sorting device, the computer must make the decision about which specifications fit a given sample. A numerical value must be assigned to each sample and matched to specifications.

In the recycling industries, it may be more useful to establish a set of nominal compositions for each alloy and use rigid specifications only for rejection decisions. For example, it might be acceptable to allow some 85-5-5-5 red brass to be mixed with 88-6-1-4 tin bronze, but any scrap with high iron must be screened. A separation scheme was developed that compared the X-ray determinations to nominal values for each of the alloying components to yield comparative "probabilites" for identification. The four highest values for the probabilities of several representative samples are identified in table A-2. In every case, the identification was made with the probability of better than 0.93, although another closely related alloy in the same group may have a slightly higher identification probability. The function that was used for comparison was weighted such that approximately equal weights were given to each of the determinations of copper, zinc, tin, lead, manganese, iron, and nickel.

$$P = \frac{1}{100}\left[100 - \sum_{k=1}^{7} \frac{(N_k - O_k)}{(1 + E_k)}\right] \qquad \text{(A-2)}$$

where P = probability,

N_k = nominal value for composition of component k in weight-percent,

O_k = observed value from X-ray analysis in weight-percent,

and E_k = estimated error in the X-ray determination in weight percent.

This probability function has no theoretical justification, but empirically does provide a means of classifying alloys that gives a numerical value to how well an unknown sample compares with a set of artificial specifications and therefore could be applied to an automated system. Better estimates of the nominal values would improve the ability of this function to distinguish between classes. The nominal values used to calculate the data in table A-2 were the midpoints of the composition range for BBII alloy specifications.

TABLE A-2. - Comparative probabilities for identification of brass and bronze alloys

Nominal identification	Probabilities							
	Highest		2d		3d		4th	
9D	9D	0.973	9C	0.936	9A	0.900	9B	0.877
12A	12A	.936	9B	.896	9A	.873	2A	.867
13B	13B	.967	5B	.842	9B	.820	5A	.819
4B	4B	.986	5A	.955	4A	.934	3B	.918
5B	5B	.973	5A	.906	13B	.861	4B	.860
1B	2B	.968	1B	.968	2A	.940	1A	.936
3D	3D	.943	3E	.904	3C	.862	3A	.861
6A	6A	.968	6B	.928	8B	.849	8C	.849
7A	8A	.970	7A	.966	6C	.952	6B	.828
8C	8B	.949	8C	.949	7A	.852	6C	.832

These values were adequate to demonstrate that a sorting procedure could be developed based on a quantitative comparison between samples of unknown composition and a set of arbitrarily defined specifications. Because of the introduction of measurement error in the X-ray analysis, there will always be some conflicts in identification in the BBII classifications. In some cases, certain alloys can never be uniquely determined because the specifications overlap. This should not be a particular problem in sorting scrap because, when the compositions are so close, either classification would undoubtedly be acceptable. It is more likely that the composition of the unknown sample would fall near the nominal values for the compositions, whereas the overlap in specifications is usually at the extreme of the composition specification. The computations for the "worst case" model are given in table A-3, showing the possible conflicts in alloy identification for several X-ray analytical times.

TABLE A-3. - Conflicts in alloy identification at several X-ray analytical times

Alloy No. (BBII)	Other identifications, depending on indicated analytical time			
	600 seconds	60 seconds	10 seconds	3 seconds
1A	-	-	1B, 2B, 2C	1B, 2B, 2C
1B	2B	2B	1A, 2B	1A, 2B
2A	-	-	-	-
2B	1B	1B	1A, 1B, 2C	1A, 1B, 2C
2C	-	-	2B	1A, 1B, 2B
3A	-	-	-	-
3B	-	-	4A	4A
3C	-	-	-	3B, 3D
3D	-	-	-	3E
3E	-	-	-	-
4A	-	4B	3B, 4B	3B, 4B, 5A
4B	5A	4A, 5A	4A, 5A	4A, 5A
5A	4B	4B	4B	4A, 4B
5B	-	-	-	-
6A	6B	6B	6B	6B
6B	6A	6A, 6C	6A, 6C, 7A	6A, 6C, 7A
6C	-	6B	6B, 7A	6B, 7A, 8A
7A	-	8A	6B, 6C, 8A	6B, 6C, 8A
8A	-	7A	6C, 7A	6B, 6C, 7A, 8C
8B	8C	8C	8C	8A, 8C
8C	8B	8B	8B	8A, 8B
9A	9C, 12A	9C, 12A	9C, 12A	9C, 12A
9B	12A	12A	12A	9A, 12A
9C	9A	9A	9A, 9D, 12A	9A, 9D, 12A
9D	-	-	9C	9C
10A	-	-	-	10B
10B	-	-	-	10A, 11A
11A	-	-	-	10B, 11B
11B	-	-	-	11A
12A	9A, 9B	9A, 9B	9A, 9B, 9C	9A, 9B, 9C
13B	-	-	-	-

☆ U.S. GPO: 1974—705-551/601

INT.-BU.OF MINES,PGH.,PA. 19161