Analysis of Byzantine copper coins by X-ray methods

Tim Padfield

Abstract

Two methods of analysis are described in this article: X-ray fluorescence analysis of the uncleaned surfaces of copper coins and electron microprobe analysis of small fragments obtained by drilling into the edges of the coins.

These two X-ray analytical methods are inaccurate when used in this way because the surface of a coin is chemically altered by corrosion and the interior is generally not chemically homogeneous. On the other hand, they damage the coin very little. X-rays discolour some minerals, though this phenomenon is rarely, if ever, observed on coins. The damage done by drilling depends entirely on the skill of the analyst, because the electron microprobe can analyse a fragment one hundredth of a millimetre across.

These advantages of minimal damage are useful in exploratory work where the expected return in information would not justify the destruction or multilation of large numbers of coins for the sake of a more accurage analysis. In this report 83 coins were analysed for tin, zinc, iron, cobalt, nickel, silver, lead, antimony, arsenic and cobalt.

A numismatic analysis of the results by Philip Grierson failed to show systematic chemical differences attributable to the source of the metal but produced one interesting monetary insight: the four pentanummia of Constantinople and Nicomedia are bronze, in contrast to the higher denominations from the same mints which are copper.

ANALYSIS OF BYZANTINE COPPER COINS BY X-RAY METHODS

BY

TIM PADFIELD

with a Numismatic Commentary by

PHILIP GRIERSON

Analysis of Byzantine Copper Coins by X-ray Methods

TIM PADFIELD

Two methods of analysis are described in this article: X-ray fluorescence analysis of the uncleaned surfaces of copper coins and electron microprobe analysis of small fragments obtained by drilling into the edges of the coins.

These two X-ray analytical methods are inaccurate when used in this way because the surface of a coin is chemically altered by corrosion and the interior is generally not chemically homogeneous. On the other hand, they damage the coin very little. X-rays discolour some minerals, though this phenomenon is rarely, if ever, observed on coins. The damage done by drilling depends entirely on the skill of the analyst because the electron microprobe can analyse a fragment one hundredth of a millimetre across.

These advantages of minimal damage are useful in exploratory work where the expected return in information would not justify the destruction or mutilation of large numbers of coins for the sake of a more accurate analysis.
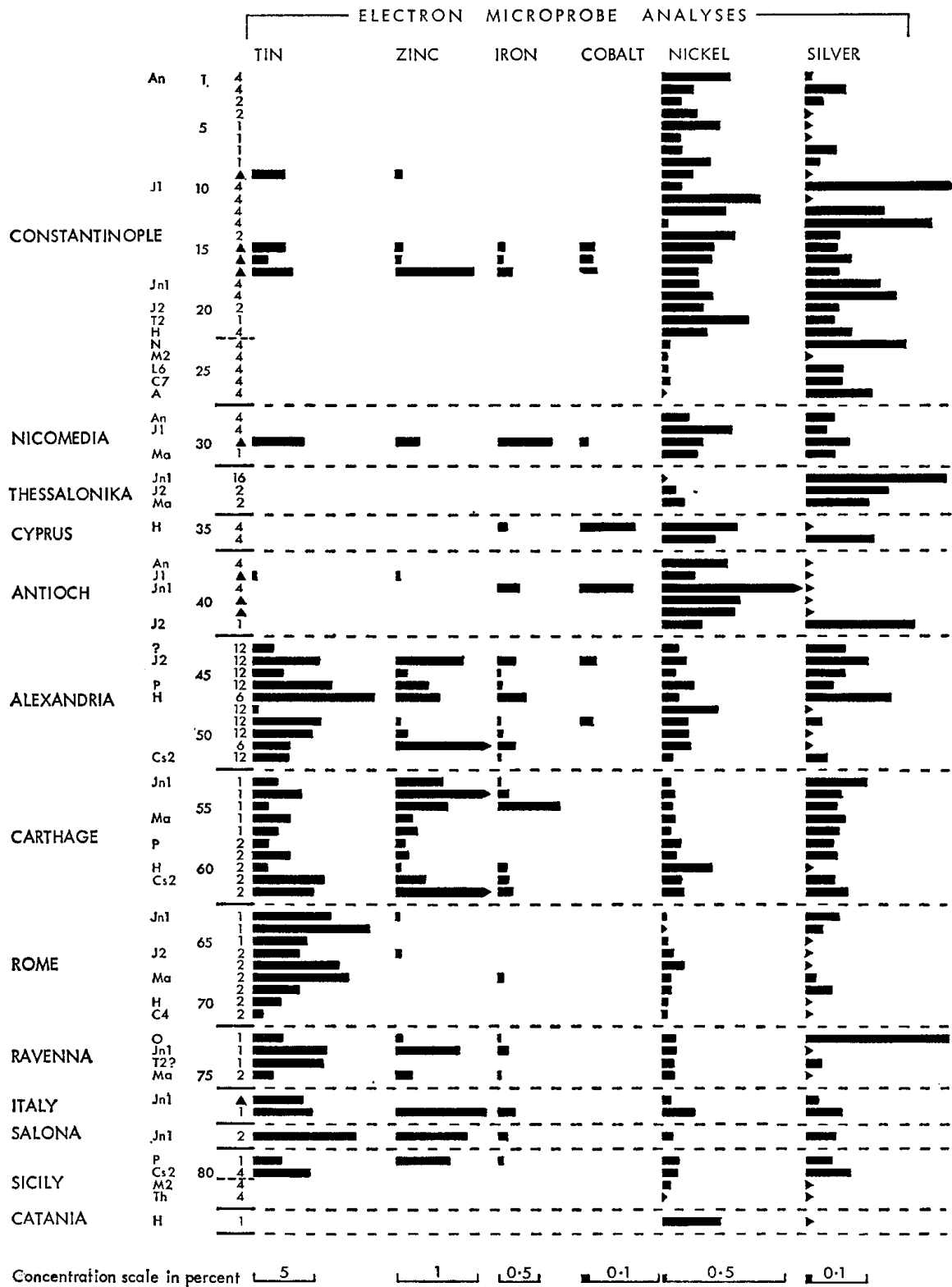
THE BYZANTINE COPPER-BASED COINAGE

Grierson, using qualitative spark spectroscopy, detected certain patterns in the abundances of minor elements in the copper coins from various Byzantine mints. These regularities were confirmed but modified by Butler and Metcalf using semi-quantitative X-ray fluorescence. The work reported here is an attempt to determine quantitatively the sharpness of these regional patterns and to extend the analysis to other elements.
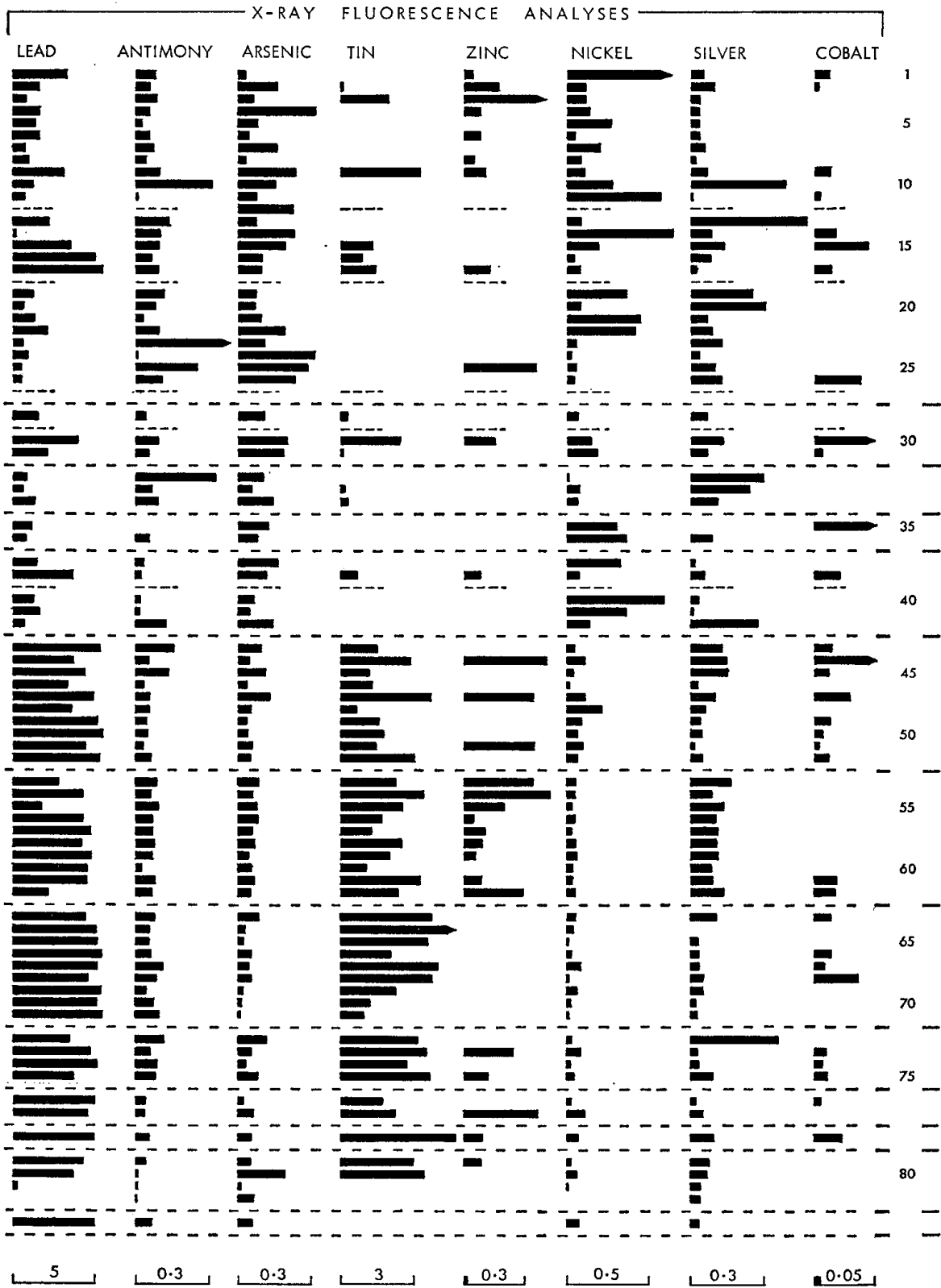
The results are tabulated in **Fig. 1**. They confirm the existence of regional patterns and even of patterns characteristic of a single mint or a single denomination. Indeed some of the regularities are so well defined that a more sensitive and accurate method of analysis might sharpen the pattern and bring out subtler details.

Fig. 1. (*Overleaf.*) The analytical results. From the left: list of mints. Emperors: Anastasius I, Justin I, Justinian I, Justin II, Tiberius II, Heraclius, Nicephorus I, Michael II, Leo VI, Constantine VII, Anon Class A, Maurice, Phocas, Constans II, Constantine IV, Ostrogothic, Theophilus. The coin number is followed by the denomination in nummi: 4 = 40, 2 = 20, 1 = 10, ▲ = 5. The length of each horizontal bar represents the abundance of the element. Dotted bars indicate missing analyses (some coins do not fit inside the X-ray spectrometer). Long bars with pointed ends would exceed the available space if inserted at their proper length. Short pointed bars represent some concentration below the detection limit. Missing bars denote the same but the detection limit is too small to be represented at this scale.

ELECTRON MICROPROBE ANALYSES

		TIN	ZINC	IRON	COBALT	NICKEL	SILVER

An 1. 4
4
2
2
5 1
1
1
1
J1 10 4
4
4
4
4
CONSTANTINOPLE 15 2
4
4
4
Jnl 4
4
J2 20 4
T2 2
H 4
N 4
M2 4
L6 25 4
C7 4
A 4

NICOMEDIA
An 4
J1 4
Ma 30 1

THESSALONIKA
Jnl 16
J2 2
Ma 2

CYPRUS H 35 4
4

ANTIOCH
An 4
J1 4
Jnl 4
40 4
J2 1

ALEXANDRIA
? 12
J2 12
45 12
12
P 12
H 6
12
12
50 12
6
Cs2 12

CARTHAGE
Jnl 1
1
55 1
Ma 1
1
P 2
2
H 60 2
Cs2 2

ROME
Jnl 1
1
65 1
J2 2
Ma 2
2
H 70 2
C4 2

RAVENNA
O 1
Jnl 1
T2? 1
Ma 75 2

ITALY Jnl 1

SALONA Jnl 2

SICILY
P 1
Cs2 80 4
M2 4
Th 4

CATANIA H 1

Concentration scale in percent   5   1   0·5   0·1   0·5   0·1

X-RAY FLUORESCENCE ANALYSES

| LEAD | ANTIMONY | ARSENIC | TIN | ZINC | NICKEL | SILVER | COBALT |

| 5 | 0·3 | 0·3 | 3 | 0·3 | 0·5 | 0·3 | 0·05 |

THE PHYSICAL PRINCIPLES OF X-RAY ANALYSIS

Every element emits a spectrum of X-rays when irradiated by X-rays or by electrons of sufficient energy. The spectrum of each element contains a unique assortment of X-rays of various but definite wavelengths. It is only necessary to separate the radiation from a complex mixture, such as a coinage alloy, into its component wavelengths to detect which elements are present. To find out how much of an element is present the intensity of one characteristic X-ray is compared with the intensity from a standard of known composition.

1 Primary beam

2 Characteristic X-rays

A X-ray fluorescence of coin

B X-ray fluorescence of thin film
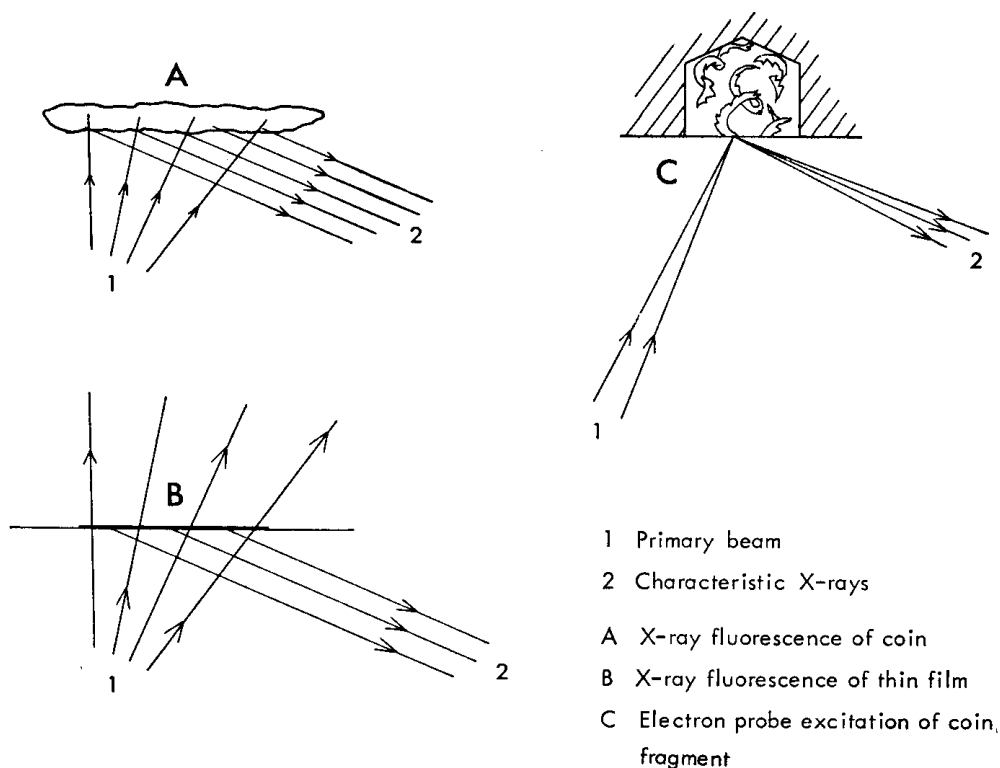
C Electron probe excitation of coin, fragment

FIG. 2. Essential features of the three analytical methods mentioned in this article.

The geometrical arrangement of incident radiation, specimen and characteristic radiation is shown in **Fig. 2**. The separation of the characteristic X-rays according to wavelength is accomplished by diffracting them from a crystal surface towards a detector, which converts X-ray photons into electrical pulses which can be counted electronically.

There are two essential differences between X-ray fluorescence and microprobe analysis. Electrons, unlike X-rays, can be focused to irradiate a very small spot on the polished surface of a small fragment of metal. On the other hand, X-ray excitation of characteristic X-rays gives about ten times better sensitivity than electron excitation.

The details of analytical procedure are summarized in a later section but one important property of X-rays, their absorption by matter, will be described at this point.

X-RAY ABSORPTION

X-rays obey Beer's law: $I = I_o e^{-\mu\rho x}$ where I_o is the X-ray intensity entering an absorbing medium of thickness x and density ρ. I is the emergent intensity, and μ is the mass absorption coefficient, which is a quantity determined only by the X-ray wavelength and by the elemental composition of the absorbing medium. An exact calculation of the depth of origin of those X-rays which reach the surface of a coin is impossible but the depth within which half the measured X-ray intensity is generated can be estimated approximately after making the assumption that the average composition of the matrix is that of Cuprite (Cu_2O), a common component of copper patina. Some of the X-rays will also pass through unoxidized copper and lead but, on the other hand, they may also pass through less absorbent minerals in the patina.

X-ray spectrometers operate on the characteristic X-rays emerging at an angle of about 30° to the specimen surface. The primary beam strikes the specimen at about 60°. In these conditions half the characteristic X-rays emerging through the coin surface will be generated within a depth given by the expression $2500/\mu\rho$ microns (one micron is one thousandth of a millimetre). This value is given for each analysed element in **Table II.** These 'half-depths' vary from 2 to 30 microns. Most patinas on ancient copper coins are much thicker than this in the depressed parts of the coin surface.

CHEMICAL COMPOSITION OF THE CORROSION LAYER

The thickness of the corrosion layer is very variable and its boundary is indefinable. Two of the coins have been sectioned by taking out with a fretsaw small discs from the more depressed and therefore more thickly patinated parts. The two coins were selected because they contained comparatively large quantities of all the analysed elements and showed different patterns of surface alteration.

These coin sections were examined with the electron microprobe. The results are presented in **Figs. 3** and **4**. These photographs are obtained by sweeping the electron beam across the specimen in a raster pattern. A synchronous electron beam scans the face of a cathode ray tube, which is photographed. The brightness of any point on the electron image is roughly proportional to the average atomic weight of the substance under the beam. In the X-ray images the density of the dark spots is proportional to the abundance of the element at that point on the specimen surface. It is clear from these photographs and from X-ray fluorescence analyses that the elements which are abundant in soils—iron, manganese, silicon, and aluminium—contaminate the corrosion layer. X-ray fluorescence analysis is, for these elements, quite uninformative. Other elements of the coin alloy, such as zinc and tin, are preferentially removed by corrosion and the analyses are inaccurate, but not unusable.

ELECTRON MICROPROBE ANALYSIS

Electron microprobe analysis of coin fragments is complicated by the inhomogeneity of the coin alloy. A molten metal mixture will cool to form a solid which may be inhomogeneous on any scale. The way in which the elements distribute themselves depends on the history of cooling and annealing and on the way in which the metal ingot is divided into individual coin blanks.
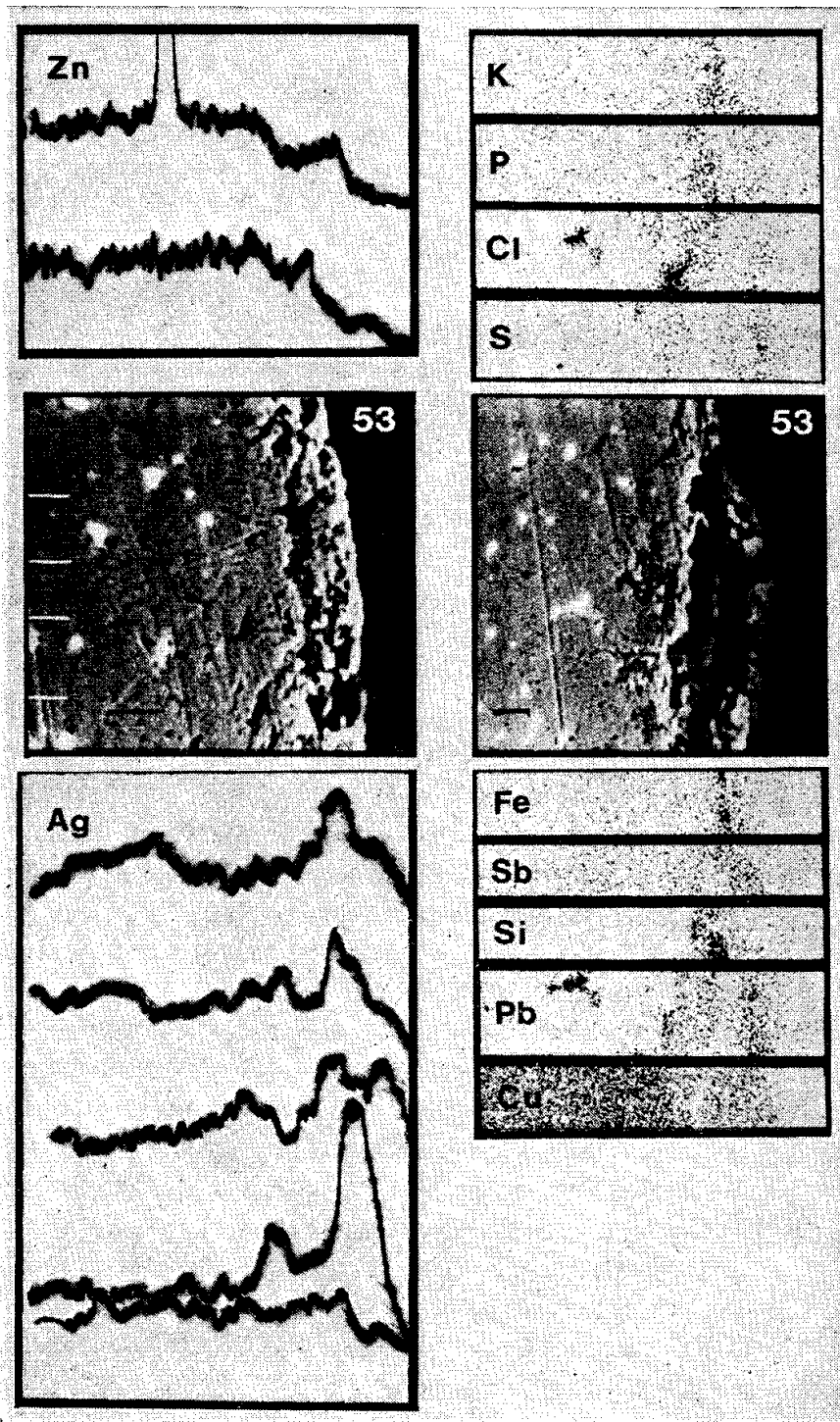
Fig. 3. Surface alteration of coin no. 53 (Carthage). The electron images are in the centre. The black bar denotes 10 microns in every photograph. Above and below, right, are composite X-ray images showing surface contamination by several elements. Top left: zinc X-ray intensity falls as the electron beam is moved horizontally across the specimen towards the surface, in two places. Bottom left: similar scans showing silver enrichment at the surface. The course of the beam across the specimen is indicated by the white bars on the electron image. The lowest trace is the background signal.

A few examples of notably inhomogeneous coins are shown in **Fig. 5**. These illustrations were chosen to show extreme segregation of the elements—most of the coins are much more uniform. Variations in composition on a larger scale have not been studied in detail but a few coins have been drilled at opposite edges and several more have been drilled deeply down a single hole to give some idea of variations between parts of the coin separated by 2 or 3 mm.
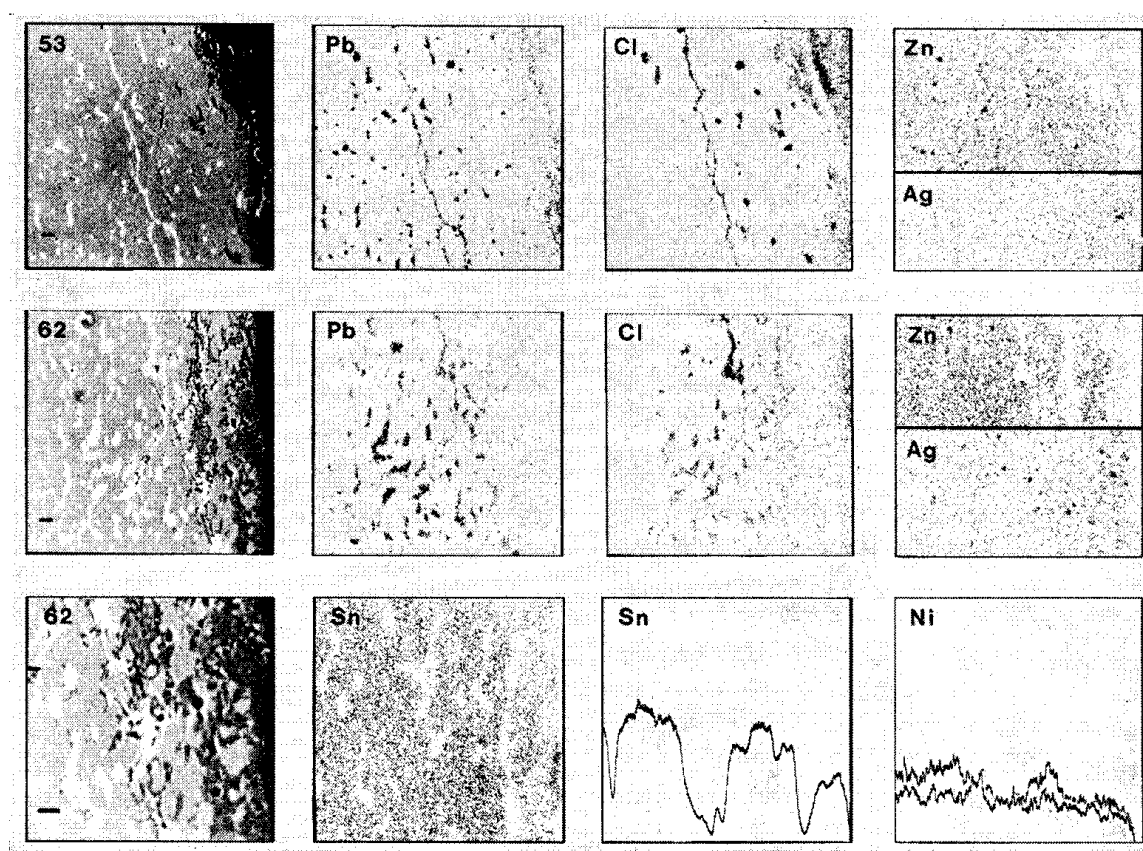

FIG. 4. Surface alteration of coins 53 and 62. The edge is on the right. The deep penetration of corrosion is shown by the distribution of chlorine, which invades the lead-rich areas to a considerable depth. Zinc also is removed from the surface and silver is either collected,·or revealed, as blobs at the surface of the coin. The surface enrichment of lead in 53 and the contrasting impoverishment in 62 is supported by the contrast between the X-ray fluorescence analyses and the scanning microprobe analyses:

No. 53: XRF 2·8 EM 1·2. No. 62: XRF 2·1 EM 4·3 per cent.

The bottom row of pictures demonstrates the impoverishment of tin and nickel in the corrosion layer of coin 62. The line of the X-ray scan is marked by a black line at the margin of the electron image. The lower trace in the nickel diagram is the background signal. The black bar denotes 10 microns.

Nearly all the coins contain a small portion, seldom more than 5 per cent, of a separate lead phase. This was not analysed and so there is a possibility that if any trace element is greatly concentrated in this phase at the expense of the copper part of the coin the analysis may seriously underestimate the abundance of this element in the whole coin.

The distribution of all the elements between these two phases could only be determined in a qualitative way because the particle sizes and the element abundances were both small. None of the analysed elements are strongly concentrated in the lead phase but the curious distribution of silver (see **Fig. 6**) gives cause for anxiety over the analytical accuracy.
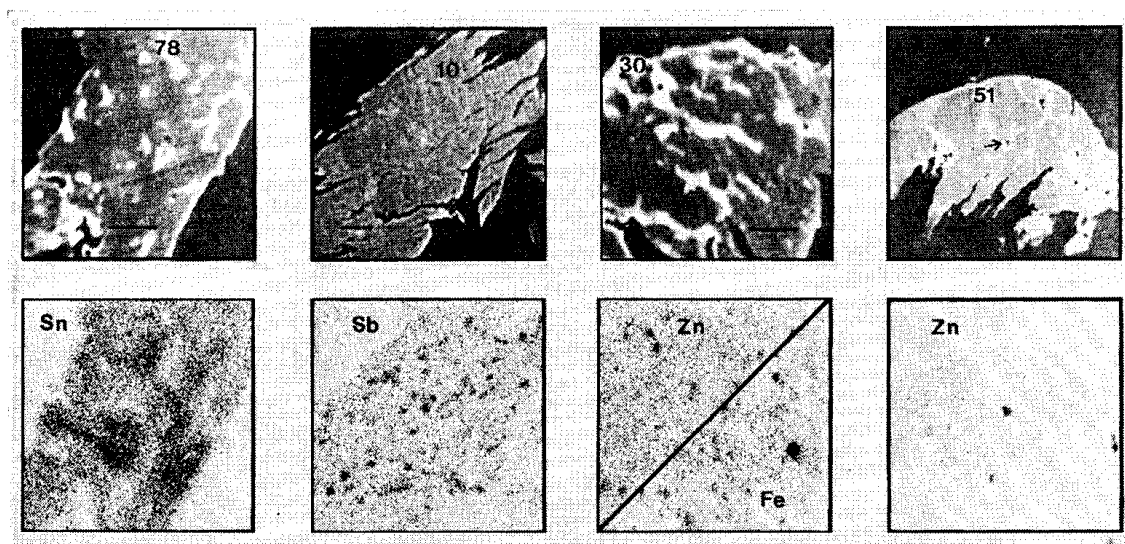

FIG. 5. The uneven distribution of the elements within coins is displayed in these examples, which represent the worst cases encountered. The pale areas in the electron images are lead rich. The zinc rich areas of 30 and 51 are within the lead. The zinc distributes itself between the copper and the lead phases when they separate. As the lead cools the zinc separates as a third phase. The coins, from left to right, are numbered 78, 10, 30, and 51 in Fig. 1. The black bar denotes 10 microns.

ANALYTICAL STRATEGY

I have used the microprobe as the main analytical tool, with the X-ray fluorescence results as a source of extra but less reliable analyses and as a check to ensure that the small microprobe samples are not totally unrepresentative of the whole coin. By using in combination two methods whose sources of error are completely different I hoped to be able to detect those microprobe analyses which were likely to be erroneous beyond the generous limits of confidence, plus or minus 30 per cent, which seemed adequate for this particular task.

The sources of error lie mainly in the coins, not in the instruments, so it is impossible to quote analytical precision and accuracy in the usual statistical way. **Table I** collects together replicate analyses of some of the coins. From these it can be seen that the microprobe tin analyses may be in error by over 50 per cent, but this turns out not to matter very much. The other elements show better reproducibility. Except when the instrument is operating close to the detection limit the precision of each determination is considerably better than the accuracy of the quoted coin analysis.

A comparison between microprobe and XRF results, **Fig. 7**, shows the expected systematic differences caused by surface impoverishment of tin, zinc and perhaps nickel, and enrichment of silver. After adjustment for these general effects it will be found that most of the analyses according to one method are not more than twice or less than half of the result produced by the other method. Some notable exceptions will be discussed in a later section.
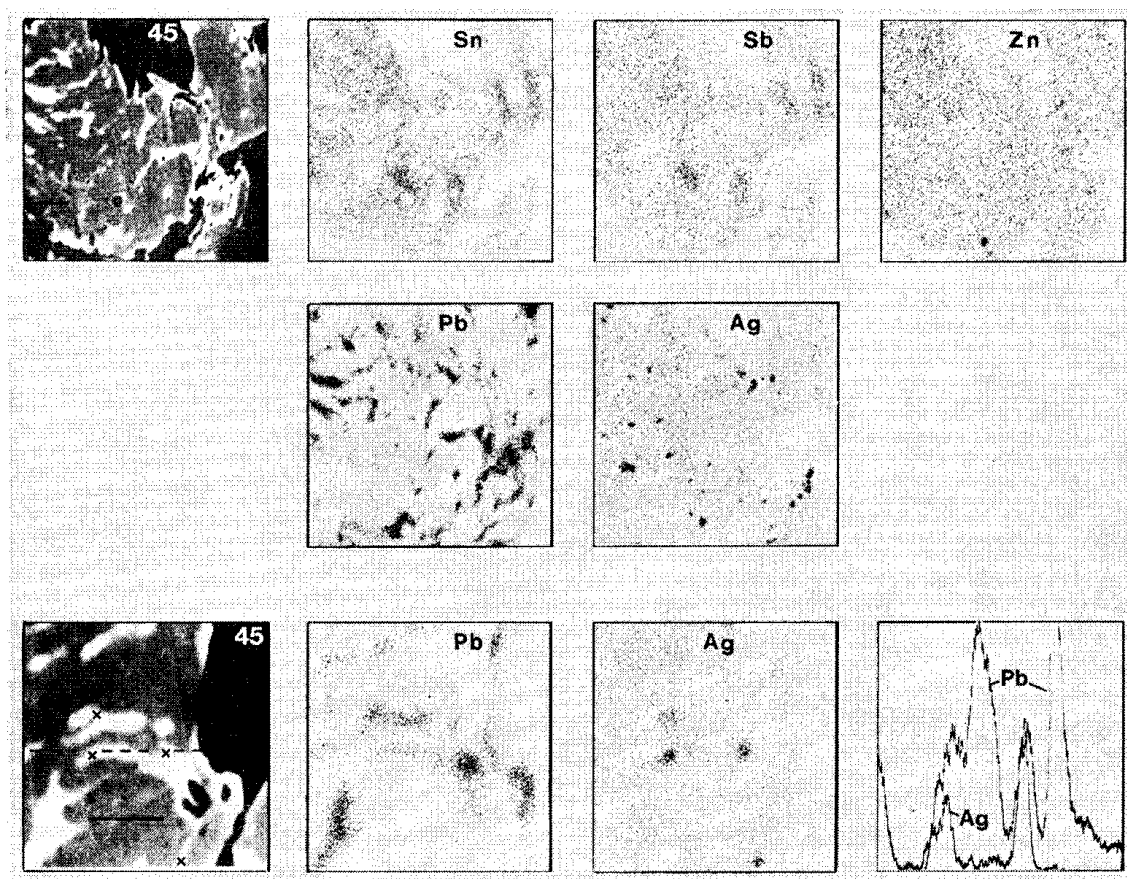

FIG. 6. The distribution of silver and other elements within coin 45. Notice the similarity of tin and antimony distributions. Silver is often found as separate particles within the lead phase. The bottom row of pictures shows, at higher magnification, the distributions of lead and silver. Silver high spots are marked on the electron image together with the path of the X-ray scans. The black bar denotes 10 microns.

VALIDITY AND USEFULNESS OF THESE ANALYTICAL METHODS

A glance at the accumulated results shown in Fig. 1 reveals some very marked patterns of minor element abundances. These will be discussed in detail later but it is immediately apparent that some of the groups of coins—those from Antioch, Carthage, and Rome, for example, show a uniformity of composition better than the analytical confidence limits. This does not necessarily mean that these uniformities are accidental, because the confidence limits are based on results from those coins which proved most difficult
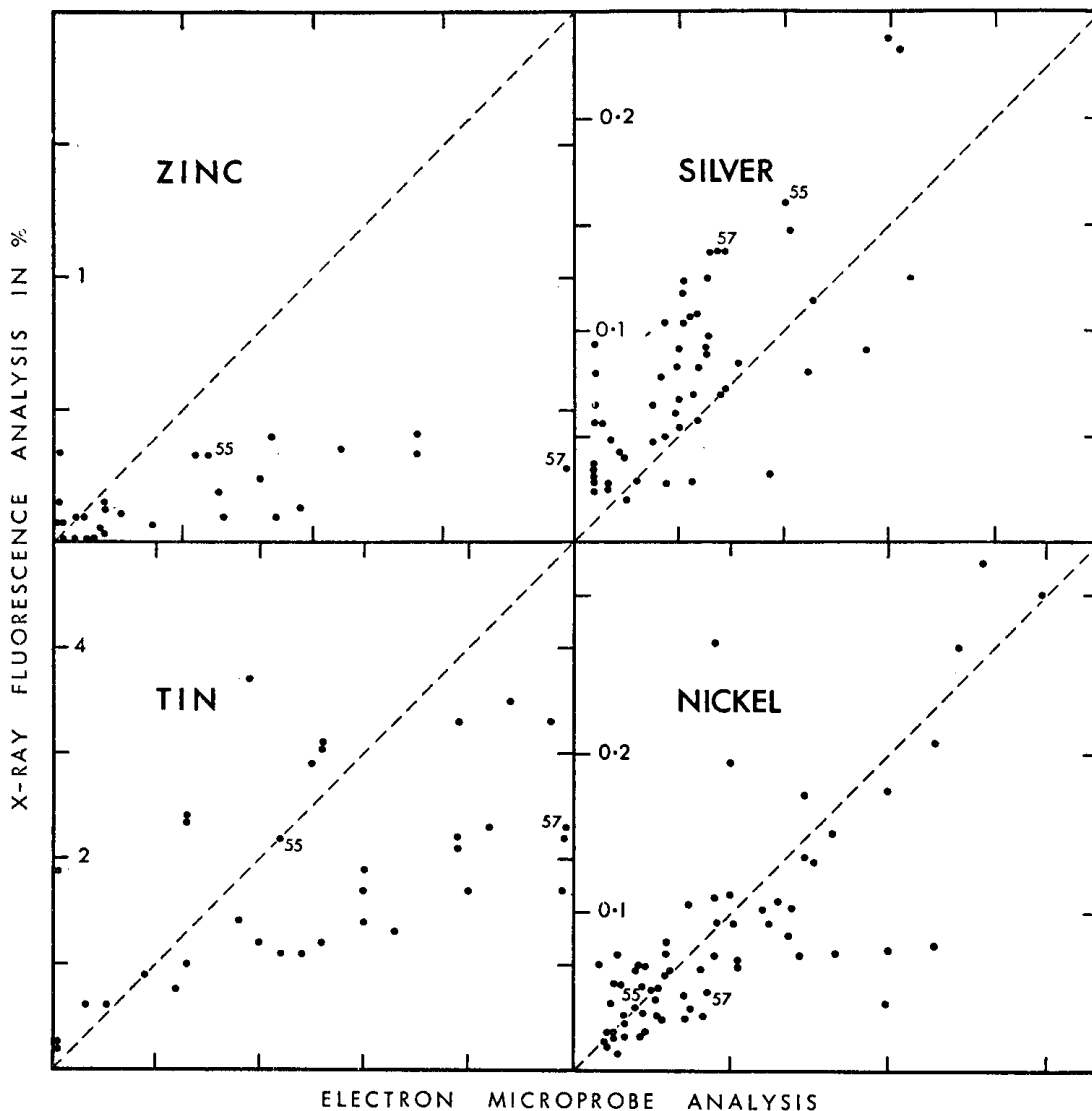
FIG. 7. A comparison between X-ray fluorescence analyses (plotted vertically) and electron micro-probe analyses (plotted horizontally). The two scales are identical and the dotted line indicates equality of the two results. The surface impoverishment of zinc and tin are clearly revealed. Silver is enriched and nickel very slightly impoverished. The points representing the two sectioned coins, 53 and 62, are marked on the diagram as 55 and 57 respectively.

to analyse. Nevertheless, it is clear now that I should have chosen a more accurate method (to measure the uniformly low nickel and silver of Rome) and a more sensitive method (to measure the silver of Antioch).

On the other hand, even the unreliable X-ray fluorescence analyses show, with a single important exception, that the coins from the mints of the north-eastern Mediterranean are copper, except for the pentanummia of Constantinople and Nicomedia which are bronze. All the others, except for some late Sicilian coins, are bronze. More subtle

regularities can be suspected, though not proved, from the XRF analyses of other elements such as arsenic (high in the north-eastern coins) and zinc (abundant in Carthaginian coins, absent in coins of the Rome mint).

It is worth considering therefore whether a more accurate method of X-ray analysis could be developed. The very small penetration of the fluorescent X-rays, between 2 and 30 microns through cuprous oxide, suggests that a small quantity of fresh metal drilled from the interior of a coin could be presented to the spectrometer as a thin film. This thin film analysis (B in Fig. 2) would overcome nearly all the problems which beset the methods already described, without a serious loss of sensitivity. The detection limit is about a tenth of a microgram for most of the elements mentioned in this article. An optimum charge of about 5 mg. of metal could therefore be analysed down to a detection limit of less than 100 ppm. Some preliminary experiments give hope that such a method may soon be made to work.

The X-ray milliprobe, described elsewhere in this volume, should be capable of similar sensitivity.

INTERPRETATION OF THE RESULTS

Fig. 1 presents a complicated set of results compounded from analytical errors, natural variations in ore deposits, and different methods of extracting metal from those ores. To these sources of variation can be added the effects of mixing two metals, copper and tin, from different sources. The lead also may contribute as well as absorb its quota of minor elements. Information of a different sort comes from the microprobe observation of the distribution of the elements within a single specimen. Some further information may yet be gleaned from metallographic study of the coin fragments.

A detailed dissection of the analyses must wait upon further results—some mints are represented by very few coins and some large time gaps interrupt the sequence. I have not yet assembled the available information on the geographical distribution of minor elements in ore deposits or on the effects of various smelting and alloying techniques.

However, a few interesting facts can be extracted at this early stage:

1. The pentanummia of Constantinople and Nicomedia are bronze. All other denominations are copper. The very small tin content of no. 38 from Antioch and the absence of tin in 40 and 41 suggests that Antioch did not conform to this custom.

2. All the coins from mints outside Greece, Asia Minor, Cyprus, and Syria are bronze except for two late Sicilian coins and the single coin from Catania.

3. Tin, zinc, and iron are usually present together. Zinc and tin are usually either abundant or undetectable. Nearly all the iron-bearing coins contain zinc. The Roman coins contain tin with very low zinc and iron. These facts can perhaps be attributed to varying smelting practice. Copper can be purified from zinc and iron by controlled oxidation of the molten metal, bronze cannot be purified in this way.

4. The bronzes contain much more lead than the coppers.

5. The Carthaginian coins contain comparatively high concentrations of zinc.

6. The late Sicilian coins 81 and 82 are unusually pure.

These variations in compositions are probably due to differences in government policy and in foundry practice. There are other compositional peculiarities which probably reflect the composition of the ore:

7. High nickel values are characteristic of the north-eastern group of mints. Exceptions are the coins of Thessalonica and the later coins of Constantinople. Low nickel values are characteristic of the Italian peninsula.

8. The silver abundances, in spite of analytical problems, show several interesting regularities. Early coins of Constantinople have low silver. Later there comes a group with medium to high silver. The coins from Antioch and Rome are mostly low in silver.

9. Antimony is low in coins from Antioch and Sicily.

10. Arsenic is high in the north-eastern group. Notice particularly the high arsenic in the late coins of Constantinople.

11. Cobalt, the most difficult element to determine because of its low concentration, has a very intriguing distribution. There are two coins with unusually high cobalt content: 35 (Cyprus) and 39 (Antioch). These coins are very similar in the presence of iron without tin, high nickel and low silver. Unfortunately there are no similarities except in composition!

The microprobe results suggest that cobalt is more abundant in the few bronzes from Constantinople and Nicomedia. XRF results, however, blur the pattern. Confirmation of this distribution would strongly suggest a different source of tin for these two mints.

These are the most evident regularities of composition taken element by element. The individual mints show compositional patterns based on the abundances of several elements:

12. Constantinople: The earlier copper coins are marked by moderate nickel concentration, low silver and, for copper coins, an unusually high abundance of lead, zinc, and sometimes tin in the XRF results. One of the coins (3) gives less than 200 ppm zinc according to microprobe analysis but 1·6 per cent zinc by XRF analysis—the largest discrepancy in the entire set of analyses.

Later coins from this mint have a dominant pattern of high nickel and silver concentrations with moderately high arsenic. This set of coins is followed much later by a group (23–7) with low nickel and high arsenic.

13. The coins from Nicomedia would fit without disturbance among the coins of Constantinople.

14. Coins from Thessalonica show low nickel and high silver, but their number is too small to allow any discussion of the significance of the analyses. The same argument applies to the coins from Cyprus.

15. Antioch provides a pattern of coin composition that makes one wish for more analyses. There is evidence from four of the six coins of a characteristic group with low silver and antimony and high nickel. The other two coins disturb the pattern.

16. Alexandrian coins present minor element abundances notable only for their variability.

17. Carthage presents a rather consistent pattern of high zinc, low nickel, high silver, and moderate arsenic.

18. Rome is characterized by the absence of minor elements. Tin and lead are abundant but nickel, silver, and arsenic are all low. This is the best defined group of coins. The coins from other Italian mints present a similar character except for a more variable zinc and iron content.

The explanation of these regularities is a task for the future. The geographical distribution of the mines and the chemical characteristics of their ore, the processes of smelting, of purifying, alloying, and casting, all influence the chemical composition of these coins.

A SUMMARY OF SPECIMEN PREPARATION AND ANALYTICAL PROCEDURES

The coins were not treated in any way before X-ray fluorescence analysis. The Philips PW 1212 spectrometer holds specimens horizontally over the X-ray source and spins them. The coins were laid on 6 micron polyester film stretched over the base of the specimen holder. The smaller coins were held in the middle of the irradiated area by a small dab of 'Cow Gum' on the plastic film.

X-ray intensities were measured with the spectrometer tuned to the spectral line of the element and also at one or two near-by background positions. The ratio of peak intensity to background is assumed to be proportional to the abundance of the element in the specimen. This ratio method compensates, to some extent, for the variation in size of the coins and for the variation in absorbing power of the patina within which many of the X-rays are generated. The method also has the important advantage of allowing the use of standards made not from metal, which is very difficult to make homogeneous, but from finely powdered oxides of the various elements mixed into a base of spectrographically pure cupric oxide.

The analytical conditions for each element are set out in **Table II**. A scintillation counter, pulse height discriminator, and pulse counter were used for all elements. The counting time was 20 seconds for all elements and backgrounds except cobalt which needed 40 seconds. All count times were split into two sessions to detect instrument errors.

There are no particular difficulties in analysis for any of the elements. The zinc $K\alpha$ suffers interference from copper, and the zinc $K\beta$ is very strongly absorbed by copper. This accounts for the poor detection limit and the sensitivity to surface impoverishment of zinc shown in Fig. 7.

ELECTRON MICROPROBE ANALYSES

This analytical method is similar in many ways to X-ray fluorescence. The essential difference is that the characteristic X-rays of the elements are excited by an electron beam directed at the polished surface of the metal. The intensity of the characteristic X-radiation from an element within an alloy is approximately proportional to its concentration. The analysis can be refined by the application of correction procedures based on theoretical calculations of the efficiency of production and absorption of the X-rays.

Unlike X-ray fluorescence, pure elements or their simple compounds may be used as standards to determine traces of elements. The correction factors and other analytical conditions are listed in Table II.

Fragments of uncorroded metal were obtained by drilling into the edge of each coin. The volume sampled in this way was a cylinder about 0·5 mm. deep by 0·8 mm. diameter. One face of a pure copper block of 1 cm. edge was drilled with an array of 1 mm. diameter holes, each about 1 mm. deep. The holes were filled with a liquid epoxy resin (Shell Epikote 815 with hardener Epikure RTU). The fragments from each coin were loaded into separate holes with a needle made sticky with the resin. When the resin had set hard the copper blocks were polished by hand on lead laps (or tin laps for lead analysis). Cloth and paper polishing surfaces cause rounding of the surfaces of the tiny fragments, which vitiates the analysis. Boron carbide was the abrasive. The final polish used 2-micron particles. The lubricant was a mixture of grease, light oil, and paraffin in the ratio 1:3:5. The polished block was vacuum coated with carbon to provide a conducting surface which allows the electrons to escape from the isolated copper fragments during irradiation.

The electron microprobe used was an A.E.I. SEM 2 instrument. An electron beam of 0·2 microamps of 30 KeV electrons, focused to a point about 1 micron across, was used to generate the X-rays. Because the coins are inhomogeneous at least five separate determinations were made on five different fragments. If these results showed a large scatter several more points were analysed. Sometimes it was possible to compensate for inhomogeneity by moving the beam over the specimen during the measurement but many coins contain a finely disseminated lead phase which prevented this.

The electron microprobe is inherently less sensitive than X-ray fluorescence. The detection limit is about 100 parts per million for most of the analysed elements. The time taken for a single analysis was between 1 minute (for tin) and 10 minutes (for cobalt).

Acknowledgement

References and Bibliography

Previous work on the composition of the Byzantine copper coinage:

P. GRIERSON, 'Trace elements in Byzantine copper coins of the 6th and 7th centuries', *Dona Numismatica*, Hamburg, 1965, pp. 29–35.

B. C. M. BUTLER and D. M. METCALF, 'Trace elements in Byzantine copper coins: a method of non-destructive analysis', *NCirc* LXXV (1967), 229–34.

Useful texts on X-ray analytical methods:

R. JENKINS and J. L. DE VRIES, *Practical X-ray Spectrometry*, Eindhoven, 1967.

R. O. MÜLLER, *Spektrochemische Analysen mit Röntgenfluoreszenz*, Munich, 1967.

J. ZUSSMAN (editor), *Physical Methods in Determinative Mineralogy*, London, 1967. This book contains articles on X-ray fluorescence spectrography by K. Norrish and B. W. Chappell (pp. 161–214), and on electron probe microanalysis by J. V. P. Long (pp. 215–60).

TABLE I
Analytical precision

	Tin	Zinc	Iron	Cobalt	Nickel	Silver	Lead	Antimony	Arsenic
Electron microprobe									
Constantinople 10						3,600 3,500			
15					770 940	2,400 560			
16*	1·2 1·1 1·4		630 630		2,070 1,950	720 700 750			
26*			550 670 730	130 140 120	2,090 1,860 2,030	460 680			
Nicomedia 30	3·9 4·6	5,000 1,700	5,700 7,200		410 310	690 750			
Cyprus 35				610 740	1,620 1,670				
					2,700 3,200				
Alexandria 45*	1·8 2·9 2·9	2,600 2,000	290 210 240		660 410 510	660 380 630			
Carthage 53*	2·2 2·0	5,700 6,050	200 240		415 480	930 1,050			
60*	1·3 1·3 1·4	680 650	940 990 1,020		1,600 2,060 2,200				
62*	5·2 4·9	2,000 2,500	1,600 1,800		860 850	600 770			
Salona 78	8·6 8·5	8,600 8,700	1,200 800		410 460	530 440			
X-ray fluorescence									
Constantinople 11*									
17	1·3 1·3		6,200 6,500	110 120	710 720	300 280		950 900	920 760
22*									1,870 1,930
24*									3,170 3,130
Antioch 37	0·01 0·01		1,500 940	(7) (20)	3,370 3,160	170 210	1·4 1·4		
Cyprus 36								350 390	
Alexandria 43								810 780	
								910 910	
49*	1·5 1·7		780 780 670	150 130 140	860 870 980	380 370 460	5·0 5·1 5·1	410 420 480	
Carthage 54*	3·2 3·3 3·3		4,700 4,900 4,500	30 40 40	520 520 510	810 840 800	4·1 4·2 4·2	610 630 650	
Rome 68*	3·8 3·7 3·7		880 950 660	320 350 400	220 240 190	550 550 610	4·7 4·5 4·6	890 860 840	
Ravenna 73									
Italy 76	1·7 1·7	2,200 2,400	1,300 1,300	110 50	350 280	220 290	5·1 5·0	370 410	

Replicate analyses. All figures are in parts per million except tin and lead which are in per cent. An asterisk by a coin number indicates that the last figure of each set comes from the opposite edge (microprobe) or the opposite face (XRF) of the coin. The coins used for testing microprobe reproducibility are not a random sample—most of these coins were re-analysed because of the variability of the X-ray signal over the polished surface.

TABLE II

Analytical conditions

Element	Electron microprobe				X-ray fluorescence				
	X-ray	Crystal	Detection limit in ppm	Correction factor	Target	X-ray	Crystal	Detection limit in ppm	Penetration in microns
Tin	$L\alpha$	PE	200	1·3	W	$K\alpha$	LiF 220	40	25
Zinc	$K\alpha$	LiF	200	1·0	Ag	$K\beta$	LiF	200	2
Iron	$K\alpha$	LiF	150	0·8					
Cobalt	$K\alpha$	LiF	100	0·74	W	$K\alpha$	LiF	50	6
Nickel	$K\alpha$	LiF	150	0·9	W	$K\alpha$	LiF	20	7
Silver	$L\alpha$	PE	100	1·4	W	$K\alpha$	LiF 220	50	20
Lead	$M\alpha$	PE			W	$L\beta$	LiF	100	4
Antimony	$L\alpha$	PE			W	$K\alpha$	LiF 220	30	30
Arsenic					Ag	$K\beta$	LiF	60	3

Electron beam 30 KV 0·2 μA X-ray take off angle is about 22·5° to plane of specimen.
The microprobe correction factor corrects the crude analysis based on the intensity ratio to the pure metal standard.
PE = Pentaerythritol, LiF = lithium fluoride cleaved in 200 plane.
X-ray generator 60 KV, 24 mA for silver target, 32 mA for Tungsten.

Numismatic Commentary

PHILIP GRIERSON

AN inquiry of this kind is almost bound to raise as many problems as it settles, since it makes plain the areas for which further information is required. The most important single novelty in Mr. Padfield's results is the fact that the four pentanummia of Constantinople and Nicomedia which were analysed are of bronze, in contrast to the higher denominations of the same mints, which are of copper. This difference is not apparent from the outward appearance of the coins, patination having rendered them all alike. The coins in question are of either Anastasius I or Justin I. Bibra also reported a few coins of Justin I, Justinian I, and Maurice as being of bronze, and though he does not state either their denominations or their mints, their weights show that they must also have been pentanummia. One would like to have more material, but the chronological spread from Anastasius I to Maurice indicates fairly clearly that the composition of the pentanummia of Constantinople and Nicomedia was systematically differentiated from that of other denominations.

This remarkable phenomenon is probably to be explained by the circumstances in which the pentanummium came into existence as a denomination. It was added during the reign of Anastasius I to the pattern of multiples when the weights of these were doubled. The follis of the new series had probably a theoretical weight of 16·4 g., implying a decanummium of just over 4 g. A pentanummium of proportionate weight would have been a coin of 2 g., i.e. only twice the weight of the nummus. So considerable a disparity between the proportions of weight and value could not be overlooked for the pentanummium in the way that it was for the higher multiples of the nummus. The difficulty was apparently solved by making the new coin of what was technically a different and more valuable 'metal', in much the same way as the old dupondius had been differentiated from the as. The device may be compared with the use of brass for the threepenny piece used in Britain between 1937 and 1971, which was actually lighter than the bronze penny—6·7 g. as against 9·4 g.—one-third its value. Here the coins have remained quite distinct in colour, but this results from the modern trick of adding a small percentage of nickel to the brass alloy in order to prevent oxidation and the consequent browning of the surface.

The use of bronze for the pentanummia was limited, on the evidence so far available, to the mints of Constantinople and Nicomedia, but one would expect it for Cyzicus also. On the evidence of three pentanummia it was not the practice at Antioch, though one would like more evidence on the point.

The fact that pentanummia can be of a different metallic composition from other subsidiary coins of the same mint has one unfortunate consequence, for it means that differences in composition do not necessarily, as was originally hoped, imply differences in mint. That they sometimes do so is clear, however, and the study of further coins should show under what circumstances such differences remain a valid criterion and under what others they give ambiguous or negative results.

ABBREVIATIONS

AJA	*American Journal of Archaeology*
ANSMN	*American Numismatic Society Museum Notes*
ANSNS	*American Numismatic Society Numismatic Studies*
BMC	*British Museum Catalogue*
BNJ	*British Numismatic Journal*
BSFN	*Bulletin de la société française de numismatique*
DOC	*Dumbarton Oaks Catalogue*
HBN	*Hamburger Beiträge zur Numismatik*
IMC	*Indian Museum Catalogue*
JESHO	*Journal of Economic and Social History of the Orient*
JMP	*Jaarboek voor Munt- en Penningkunde*
JNG	*Jahrbuch für Numismatik und Geldgeschichte*
JNSI	*Journal of the Numismatic Society of India*
JRS	*Journal of Roman Studies*
MBNG	*Mitteilungen der Bayerischen numismatischen Gesellschaft*
NC	*Numismatic Chronicle*
NCirc	*Numismatic Circular*
NNÅ	*Nordisk Numismatic Årsskrift*
NNM	*Numismatic Notes and Monographs*
NNUM	*Nordisk Numismatisk Unions Medlemsblad*
NRom	*Numismatique Romaine. Essais, recherches et documents*
NS	*Numismatický Sborník*
NZ	*Numismatische Zeitschrift*
RBN	*Revue belge de numismatique*
RIC	Mattingly, Sydenham *et al.*, *Roman Imperial Coinage*
RIN	*Rivista Italiana di Numismatica*
RN	*Revue numismatique*
SM	*Schweizer Münzblätter*
SNR	*Schweizer numismatische Rundschau*
WN	*Wiadomości Numizmatyczne*
ZfN	*Zeitschrift für Numismatik*