

X-RAY FLUORESCENT ANALYSIS APPLIED TO ARCHAEOLOGY

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ABSTRACT

X-RAY fluorescence is now a well established method of analysis both in the laboratory and industry. The fact that the method is essentially non-destructive makes it particularly attractive for the analysis of archaeological and museum artifacts. This paper gives a short simplified description of the method and gives an indication of the type of problem which may be tackled. Due to certain fundamental characteristics of the technique it is not suitable for some projects which would seem at first sight to present no problems.

SCIENTIFIC PRINCIPLES

Atoms of the different elements which compose nature are characterised according to the Bohr theory by the number of electrons which spin round the atomic nucleus. Hydrogen is the simplest since it only has one electron; an example of a more complicated atom is shown schematically in Fig. 1. It will be seen that all the electrons do not spin in one orbit (or shell) but in several which we call the K, L, M, etc. shells.

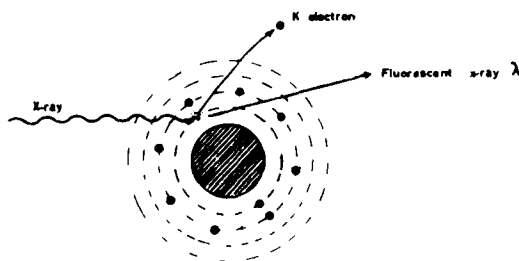


FIG. 1

The Bohr model of the atom of iron showing the electrons surrounding the nucleus. The bombarding X-rays eject a K electron and a fluorescent or characteristic X-ray quantum is generated.

When high voltage X-rays from a conventional X-ray tube (similar to the tubes used for medical radiography) strike matter some of the electrons spinning round the nucleus will be ejected from the atom. A vacant position in the K shell will be filled by an atom from another outer shell. When this happens there is an excess of energy available which must be dissipated. The atom achieves this by ejecting a characteristic or fluorescent X-ray. This X-ray will have a definite energy or wavelength since it was generated by the difference of two discrete energy levels in the atom. This energy will be different for each atom. Moreover, since there are more than two shells in most atoms several possibilities can occur within a particular type of atom or element, with the result that each element will produce fluorescent X-rays of several but definite wavelengths. In fact we are concerned with two series of lines, the K series and the L series, depending on which shell is involved.

The net practical result of this bombardment of a sample with "primary" X-rays is that we get evolved a number of "secondary" fluorescent rays of definite energy. Now all we have to do, in order that we can tell what composed the original sample, is to analyse the energies contained in the secondary beam, since we know from previous experiment the energies of fluorescent radiation from all elements. Fig. 2 shows the arrangement we use to "sort out" the different energies — an X-ray spectrometer.

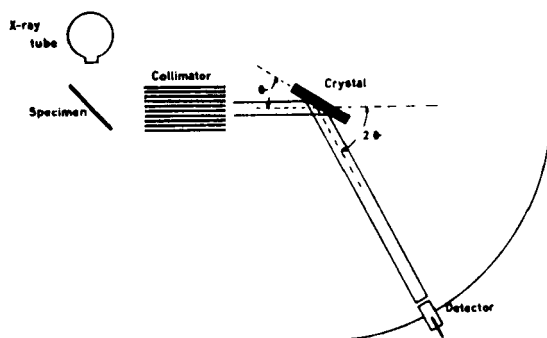


FIG. 2

The elementary X-ray spectrometer. If d = the interplanar spacing of the crystal and λ = the incident wavelength of the radiation striking it, Bragg's Law states $\lambda = 2d\sin\theta$.

To explain its method of operation it is necessary to understand Bragg's Law. When a parallel beam of X-rays of a definite energy or wavelength strikes a crystal, which one can think of as a series of planes parallel to each other, they will generally speaking be scattered in all directions or absorbed. But if the crystal happens to be turned to the Bragg angle (for that crystal and the incident X-ray wavelength) a certain proportion of the incident rays will be reflected as though the crystal surface was a mirror. Bragg's Law states that

$$\lambda = 2d\sin\theta$$

where λ = the incident wavelength

d = the distance apart of the crystal planes

θ = the angle the crystal plane makes with the incident radiation.

The value of 'd' will depend on the type of crystal used and will stay constant. Therefore we will get a reflection angle for each fluorescent energy of each element.

Our X-ray spectrometer (Fig. 2) will consist of several components. The X-ray tube gives out high energy radiation which bombards the specimen which in turn produces fluorescent radiation. This is collimated by a number of parallel slits so that the beam emerging will also be essentially parallel. The collimated beam will strike the crystal and if the latter is at the Bragg angle for a portion of the incident radiation that portion will be reflected into the detector. The detector, which may consist of a number of different types of counter (Geiger, photomultiplier, etc.),

will feed an electrical pulse to the recording electronics every time an X-ray quantum is reflected into it.

Let us assume that we are examining a coin, the composition of which is entirely unknown. We place the coin in the sample chamber and turn on the X-rays. We start off with the crystal and detector in line with the collimator slits and feed the output of the detector to a "ratemeter" which will record the number of pulses per second received. We now slowly turn the crystal and the detector (the latter at twice the speed of the former, so that it is always in a position to receive the reflected radiation) and record a graph of counts per second plotted against the angle of the crystal. The type of graph produced will look like Fig. 3. The position of the various peaks will identify the element concerned, whereas the height of the peak will tell us the percentage of that element present.

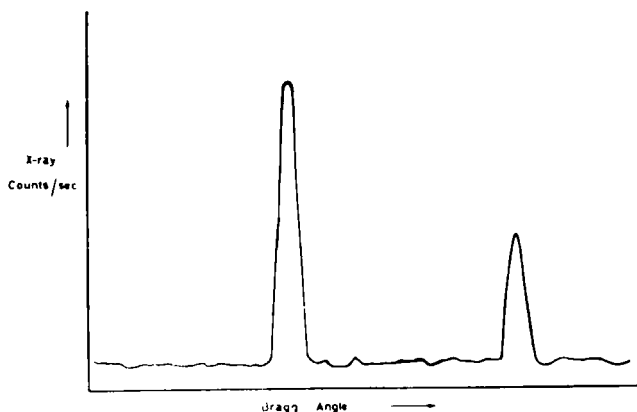


FIG. 3

An X-ray spectrum. The position of a peak will identify the element (qualitative analysis) while the height of the peak will signify the percentage present (quantitative analysis).

The foregoing gives some idea of the principles of the method, I hope particularly to the non-scientific reader. I have deliberately not complicated the issue by detailing the various electronic features, automatic devices, and methods of presentation of results. I would refer the reader, if he is interested, to other more comprehensive literature^{1, 2, 3}. There are a number of relevant observations, however, which should be understood if an estimate is to be made of the value of the technique for a particular study.

RANGE OF ELEMENTS

The most easily measured fluorescent radiation will be that which will easily penetrate the air between the specimen and the detector and also the window of the detector. Some radiation will be too soft (unenergetic) to do this and we will have to work in a vacuum and use very thin windows on our detectors. Some radiations will be too soft to be measured at all. We can therefore divide the elements in the periodic table into a number of groups and give some idea of the limits of detection.

<i>Elements with Atomic Number</i>	<i>Series Used</i>	<i>Detection</i>	<i>Lower Limit % of detection</i>
U(92) to Te(52)	L	Easy (air spectrometer)	0.05
Sb(51) to Ti(22)	K	" " "	0.01
Sc(21) to P(15)	K	Vacuum spectrometer necessary	0.1
Si(14) to Mg(12)	K	" " " (Yield Low)	1 to 5
Na(11) to H(1)	K	Yield too low	—

See Appendix for a list of the commoner elements.

In the table above it will be seen that analysis of carbon, oxygen and hydrogen (among other elements) is impossible. This means that analysis of organic material cannot be undertaken — unless of course we are looking for "inorganic" elements as impurities in an organic matrix. The sensitivities listed above must be very approximate and are average figures. Looking for elements of high atomic number in a matrix of low atomic number gives a much higher sensitivity than that listed. For example, 1 part in 10^7 of copper can be detected on an organic background.

The figures for sensitivity are given assuming we have available about $\frac{1}{4}$ sq. in. of surface area. If we are examining very small areas the sensitivity will fall in proportion.

The nature of the chemical combination of the elements involved will not effect the feasibility of analysis. For example the sample may be in the form of a base metal or chemically combined with other elements. For instance lead can be detected as an impurity in copper coinage, as a constituent of glass or a glaze, or even in the form of liquid tetra ethyl lead in petrol.

RADIATION DAMAGE

There is one particular danger which should be mentioned. If a glass or a glaze is given extensive irradiation from a powerful X-ray tube, radiation damage by 'F centre' formation will result. The damage consists of a dark patch where the rays have struck the specimen. It is due to knocking out electrons in the crystal structure. During the few weeks after irradiation much of the damage will disappear — the electron malformation will correct itself automatically at room temperature. There is, however, a "harder" component which does not seem to disappear even after several years. It may be dispersed by heating the specimen to 150°C for about an hour, which may or may not be permissible. The best approach is not to allow discoloration in the first place. Several minutes' exposure is required before any noticeable effect appears, and one must arrange one's analysis accordingly. This is usually quite possible.

SURFACE CONTAMINATION AND SURFACE ENRICHMENT

When we bombard a sample with primary X-radiation we will cause fluorescence at various depths, and if the sample is not homogeneous the analytical result will be very difficult to interpret. In fact nearly all the measured secondary X-rays will be representative of the composition of the first few thousandths of an inch. The surface of the object is often corroded to a greater or less extent and therefore a quantitative analysis representative of the whole may be impossible. Objects such

as glass and pottery are not particularly susceptible to this type of error, but metals, in particular bronzes, can only be investigated qualitatively unless a comparatively large portion of the surface is cleared of contamination. This is generally not tolerable and a small drilling (1 mm. in diameter) will cause less damage and will be more representative. Such drillings can be most conveniently analysed in the optical emission spectrometer⁴.

Metals which have been buried for a long time and which are apparently in excellent condition — for instance silver alloys, electrum or gold — may, however, not be entirely homogeneous. The phenomenon of surface enrichment may have taken place. At the moment little is known concerning either the nature or the cause of this phenomenon. In this Laboratory we had heard that ancient coins did sometimes exhibit inhomogeneity and our first realisation that the effect was serious was when we compared some results on Greek silver/copper coins obtained by neutron activation followed by γ -ray spectrometry⁵ with those obtained on the X-ray spectrometer. The latter showed much higher silver/copper ratios, showing that the silver was concentrating on the surface. The same has been found the case with gold/silver alloys — by X-ray spectrometry the apparent gold content is much inflated. Some preliminary examination of the gold/silver system has shown that the silver content on the very surface may be up to *three times* as large as the average composition.

The cause of the enrichment is somewhat obscure. It seems likely that the less noble metal is leached out over hundreds of years when buried in moist soil, but this is complicated by diffusion effects within the coin itself. It is possible that correction factors could be applied if the X-ray analysis was undertaken at differing excitation voltages, but a great deal of investigation must be done on the whole problem before reliable results on this type of specimen are possible. We have noticed references to the use of X-ray spectrometry applied to the analysis of ancient coinage and we wonder whether the possibilities of surface enrichment have been considered.

ANALYSIS OF IMPERIAL ROMAN DENarii

As an example of the difficulties which "surface enrichment" can bring about mention may be made of an extensive programme designed to put on a quantitative basis the debasement of the Imperial Roman coinage. Several hundred denarii from all periods were analysed on the X-ray spectrometer. Although the general trend of the copper/silver ratio was ascertained, it was also found that (a) the variation within a coin type varied between wide limits, and (b) even the coins themselves varied in apparent composition from one side to the other. On further investigation it was found that if we analysed the surface of a coin and then rubbed it down carefully on emery paper in stages the composition quickly changed during the first few thousandths of an inch until a constant composition was reached. This effect was more marked on some coins tested than others. However ratios of up to 3 to 1 (outside apparent silver content to core composition) were found.

It is obvious, therefore, that an extensive programme of investigation into this phenomenon is called for. We intend to initiate this during 1961 using the γ -ray spectrometer to give us average results and the electron probe microanalyser to give compositions in cross section; this will mean destroying a number of coins, but poor specimens can be used for the purpose. We hope by this programme to be able to shed light on the cause and extent of the process.

SUITABLE PROBLEMS

The considerations outlined above will decide the types of project — I use the word project since isolated analyses are seldom of much significance — which are most suitable for X-ray spectrometry.

When we want to know the *approximate* composition of a metal, a glass, ceramic or indeed any object, the constituents of which are above magnesium in the Periodic Table, the X-ray method presents few problems provided the percentage present is above those shown in the table above.

If, however, an *accurate* estimate of composition is desired, we have to contend with the surface and inhomogeneity phenomena outlined above. For some problems, such as the analysis of glazes and glass, an accurate result is comparatively easy to accomplish, but with corroded or surface enriched metals only a very semi-quantitative answer is possible.

There is a final point worth mentioning concerning accurate analysis of all materials. It is impossible to estimate the curve relating percentage composition to number of quanta of X-rays counted on a spectrum peak, and therefore we have to

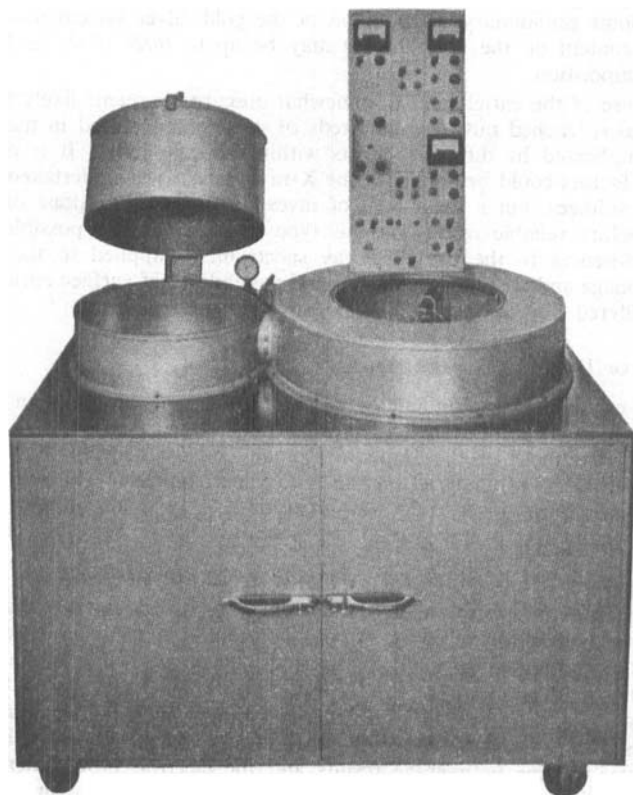


FIG. 4

The high vacuum automatic spectrometer in our Laboratory. The associated electronics are situated in another console out of the picture.

approach the problem by analysing standards of known composition. By comparing our unknowns to these standards we can deduce their composition. Reliable standards either of metal alloys, glass or ceramic material are generally either hard to find or are expensive. The Laboratory, however, is trying to collect series of such standards of various types.

REFERENCES

1. Compton A. H. and Allison S. K.: X-Rays in Theory and Experiment. Van Nostrand, New York. 1935.
2. Hall E. T.: X-ray fluorescence spectroscopy in chemical analysis. *Endeavour*, XVIII, 70. 1959.
3. Birks L. S.: X-ray Spectrochemical Analysis. Interscience, New York. 1959.
4. Brown M. A. and Blin-Stoyle A. E.: Spectrographic Analysis of British Middle and Late Bronze Age Finds. *Archaeometry* 2 Supplement. 1959
5. Emeleus V. M.: The Technique of Neutron Activation Analysis as Applied to trace element determination in pottery and coins. *Archaeometry* 1. 1958.

APPENDIX

The commoner elements arranged in order of atomic number and in groups according to the table on page 32.

Atomic No.	Element	Atomic No.	Element
1	Hydrogen	7	Nitrogen
3	Lithium	8	Oxygen
4	Beryllium	9	Fluorine
5	Boron	11	Sodium
6	Carbon		
12	Magnesium	14	Silicon
13	Aluminium		
15	Phosphorus	18	Potassium
16	Sulphur	19	Calcium
17	Chlorine	21	Scandium
22	Titanium	30	Zinc
23	Vanadium	33	Arsenic
24	Chromium	34	Selenium
25	Manganese	47	Silver
26	Iron	48	Cadmium
27	Cobalt	50	Tin
28	Nickel	51	Antimony
29	Copper		
52	Tellurium	79	Gold
53	Iodine	80	Mercury
56	Barium	82	Lead
74	Tungsten	83	Bismuth
78	Platinum	92	Uranium