CURRENT CAPABILITIES AND FUTURE GOALS IN X-RAY SPECTROSCOPY

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Abstract—After examining the main factors which govern the potential applications of X-ray fluorescent analysis, the author outlines the principal discoveries in the field of X-ray spectroscopy. Results are presented of the 10-yr Naval Research Laboratory Programme (1965-1975) which had been established for data acquisition and interpretation based on the expected advances in computer capabilities. Some of the factors which may influence X-ray analysis in the future are also considered.

INTRODUCTION
The competitive status of X-ray fluorescent analysis depends on the characteristics and limitations of the technique. Six of the salient factors are:

1. The simple relationship between characteristic X-ray wavelength and atomic number was first observed by Moseley\(^1\) in England in 1913, Fig. 1, and is the basis for easy qualitative identification of components in a sample.

2. The fact that characteristic X-ray lines represent inner shell transitions in the atom means that the wavelength and intensity are, to a first order, independent of physical state or chemical combination of the elements. This means, first, that samples can be measured as solids, powders or liquids with equal facility. Second, it means that some of the pitfalls of emission spectroscopy or atomic absorption or fluorescence are eliminated; for instance, there is no variation of intensity with time as there is in an arc; neither is there a problem with equilibrium temperature or multiple ionization states.

3. As a corollary to item 2, the close packing of atoms in solids or liquids means that interelement absorption and secondary fluorescence are much greater effects than in other methods of spectroscopy. Fortunately, mathematical formulation of these effects can be derived from physical principles.

4. The usefulness of crystals to disperse X-rays depends on the coincidence that interatomic spacings are a few Angstroms corresponding to the X-ray wavelengths. It would have been nearly impossible to construct diffraction gratings with sufficiently small spacing to disperse the X-rays.

5. The development of electronic detectors from the early days of ionization chambers and Geiger counters through to gas-proportional counters and scintillation counters has meant that one can count individual X-ray photons. This, in turn, means that the statistics and interpretation of X-ray measurements is extremely simple compared to other spectroscopic techniques. In particular, the adequacy of Si(Li) solid-state detectors to resolve the characteristic lines of neighboring elements allows much practical analysis to be carried out even without a dispersing spectrometer.

6. It is coincidental that the development of high-speed computers came about just in time to allow the necessary data treatment of interelement effects mentioned in item 3 and the necessary spectral unfolding required for the solid-state detectors mentioned in item 5.

HISTORICAL BACKGROUND
The development of X-ray spectroscopy is a fascinating story of brilliant insight combined with recognition of the fortuitous coincidences described in the previous section. It is also a story of techniques developed too soon and forgotten only to be rediscovered years later. The story is retold here briefly as a basis for understanding how we have arrived at our present capabilities and where the future may take us.

The story begins with Moseley's classic paper in 1913 pointing out the extremely simple relationship between characteristic X-ray wavelength and atomic number, Fig. 1. There were a number of important events which preceded Moseley's discovery and made it possible. (1895) Röntgen\(^2\) in Germany observed very penetrating radiation emitted from a cathode ray tube. He called it X radiation because of its unknown nature. (1908) Barkla and his colleagues\(^3\) in Britain observed that when different elements were irradiated with primary X-rays they emitted secondary radiation whose penetrating power (as measured by absorbing foils) varied from element to element. Barkla called this secondary radiation 'characteristic rays'. He also observed that this secondary radiation consisted of a 'harder' and a 'softer'

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Fig. 1. Moseley's original X-ray spectra (1913).
component which he designated as K and L radiation. He started naming in the middle of the alphabet supposing that even harder and softer components might be found later.

(1912) Beatty in Britain showed by experiment that Barkla’s ‘characteristic rays’ could be generated directly by electrons. Before Beatty’s work, it was thought they could be generated only by primary X-rays.

(1912) Freidrich and Knipping in Germany under von Laue’s supervision demonstrated that X-rays could be diffracted by crystals.

(1913) Bragg in Britain built a crystal spectrometer and recorded the X-ray spectrum from a Pt target X-ray tube (the continuum as well as the characteristic lines).

(1913) Moseley in Britain demonstrated the simple $\lambda \propto 1/Z^2$ relationship between wavelength and atomic number. Moseley commented at the time that this new spectroscopy should be very valuable for chemical analysis.

After Moseley’s publications there was a rush to measure X-ray spectra in all the universities of Europe and throughout the world. Some of the experiments which were (or could have been) important milestones were:

(1914) Maurice de Broglie in France used fluorescent excitation of the specimen outside an X-ray tube so he could examine volatile or low melting materials. For some unknown reason the advantage of de Broglie’s technique was overlooked and neglected for over 30 yr.

(1923) Coster and von Hevesy in Denmark discovered element 72 from its X-ray spectrum. It is interesting to note that Davuillier in France had previously claimed the discovery of element 72 from X-ray spectra but his lines had been shown to consist of impurity lines from several rare earths. Because of these circumstances we call element 72 Hafnium (after the Latin name for Copenhagen) rather than Cesium.

(1927) Jönsson in Sweden built a Geiger-counter spectrometer and measured X-ray tube spectra. Like de Broglie’s fluorescent excitation, Jönsson’s spectrometer was neglected and forgotten by analysts.

(1929) Eddy and Laby in Australia measured ppm trace elements in alloys by X-ray spectroscopy using photographic film to record the lines. They seemed unaware of Jönsson’s spectrometer which would have given them efficient quantitative analysis.

(1932) von Hevesy in Germany published the classic book *Chemical Analysis by X-Rays and its Applications*. In it he described the principles and techniques and suggests that it should be widely used. He gives no references to what I believe are the two critical papers, namely the ones by de Broglie and by Jönsson because they are the ones that make X-ray analysis a practical tool.

(1932–1947) No papers on chemical analysis by X-ray spectroscopy are listed in *Chemical Abstracts*. The X-ray papers during those years were concerned with more detailed fine structure in emission lines and absorption edges or with X-ray powder diffraction for identification of crystalline compounds.

Two events occurred in 1947 which were to change the course of X-ray analysis most drastically. Friedman and Birks in the United States converted a Geiger-counter diffractometer to an X-ray spectrometer for chemical analysis. Figure 2 shows the original instrument. The sample was placed outside the tube window for fluorescent excitation. Thus the forgotten efforts of de Broglie and Jönsson were resurrected and combined into what became the important field of X-ray fluorescence analysis. The second event that occurred in 1947 was Hillier’s patent for a focused electron beam to generate X-rays in a local area on a specimen and an X-ray spectrograph to measure the radiation. Fig. 3. Hillier’s concept led to the important area of electron probe microanalysis which will not be discussed in this paper.

In the 1950’s and early 1960’s there were important advances in instrumentation, specimen preparation, and data interpretation. X-ray fluorescence analysis was applied to widely ranging problems in metallurgy, geology and other disciplines. The situation which existed in 1965 can be summarized as follows:

1. Gas-proportional and scintillator detectors had replaced the Geiger counters because they could accommodate faster counting rates. The proportional and scintillator detectors also had energy-discrimination capabilities which allowed suppression of higher order diffraction lines and generally reduced background interference.

2. Regression equations had been widely accepted for relating measured X-ray intensity to quantitative composi-
tion. The equations took the form

$$C_i = R_i(1 + \Sigma \alpha_j C_j)$$

where $C_i$, $C_j$ are concentrations of element $i$ or $j$; $R_i$ is the measured relative X-ray intensity from element $i$; $\alpha_j$'s are empirical coefficients representing the effect (absorption or enhancement) of element $j$ on the intensity from element $i$. Such equations were useful for specific applications where the composition did not vary by more than about 10% from one specimen to another. The $\alpha$ coefficients had to be redetermined for each different type of specimen or for different primary radiation.

(3). Early forms of what have come to be called fundamental-parameter equations had been suggested by Shiraiwa and Fujino in Japan and by Criss in the U.S. and had been programmed on the early computers. In those equations the X-ray intensity was related to composition through analytic expressions containing mass absorption coefficients, fluorescent yields and other physical parameters.

(4). The energy dispersion method had been tested on alloy and geological specimens using the gas proportional detector but the Si(Li) solid state detector had not yet been invented.

(5). Crystals such as KAP with large interplanar spacings had been developed for measuring low Z elements from F to Ti. Metal-sterate multilayer films had also been adapted as diffracting crystals for elements from B to F.

(6). The small changes in characteristic wavelengths with valence had been used to identify the different oxidation states of S and other low Z elements.

THE 10-YR NAVAL RESEARCH LABORATORY PROGRAM AND ITS RESULTS

In about 1965 one of the Navy's consultants pointed out that computer speeds were increasing by an order of magnitude every few years and that this would have drastic effects on all kinds of data treatment and problem solving. We established a 10-yr program for data acquisition and interpretation based on the expected advances in computer capabilities. There were four principal goals in the program:

(1). Prepare the fundamental-parameters equations in optimum form for computer evaluation; develop an efficient format for the time-sharing mode and conversational mode as well as batch processing.

(2) Refine the electron transport program for X-ray generation in solids so it can be used to calculate complete X-ray tube spectral distributions on an absolute basis.

(3). Extend and/or modify crystal-diffraction theory to calculate diffraction efficiency of analyzer crystals of intermediate perfection; the crystals of concern have either naturally occurring or deliberately introduced defects in the crystal lattice.

(4). Develop mathematical expressions for X-ray absorption and secondary fluorescence in heterogeneous specimens; test them on well characterized specimens.

The 10-yr program was established as a combination of theoretical calculations and experimental verification. Work in several of the four areas moved forward simultaneously rather than sequentially. We have essentially reached all of the goals except for a complete treatment of secondary fluorescence in heterogeneous specimens. Publication of many of the results will be appearing in the literature in the near future.

Spectral distributions from X-ray tubes

The spectral distributions of continuum (bremsstrahlung) and characteristic target lines from X-ray tubes are needed as input to the fundamental-parameter equations. Figure 4 shows the latest results for a Cr target X-ray tube on an absolute intensity basis. The agreement between calculated and measured values seems to us to be amazingly good. Figure 5 shows similar results for a W target tube where there is excellent agreement on a relative basis (all that is needed for fluorescence analysis) but a small offset on an absolute basis. Figure 6 repeats earlier results obtained on a Rh target tube before the values for

![Fig. 4. Comparison of calculated and measured spectrum for Cr X-ray tube.](image)

![Fig. 5. Comparison of calculated and measured spectrum for W X-ray tube.](image)

![Fig. 6. Comparison of calculated and measured spectrum for Rh X-ray tube.](image)
cross-sections for continuum production were refined to their present values. Even for this earlier Rh spectrum the distribution was adequate for chemical analysis. Table 1 repeats the comparison between calculated and measured values for the characteristic lines from a number of targets.

We now believe that spectral distributions can be calculated with adequate accuracy for quantitative analysis and that there will be no need for further measurements. We plan to prepare tables of calculated spectra for the commonly used X-ray targets at various values of operating voltage and X-ray take-off angle. This should greatly increase the usefulness of the fundamental-parameter method to analysts.

Efficiency of analyzer crystals

The analyzer crystal is the heart of the X-ray spectrometer. An improvement of a factor of 2 in the crystal efficiency is as valuable as increasing the wattage of the X-ray tube by a factor of 2. In order to understand the relationship between diffraction efficiency and crystal perfection it was necessary to modify existing diffraction theory. Figures 7 and 8 show detailed results for two of the most commonly used crystals, LiF and KAP. In Fig. 7 for LiF the calculated values for a freshly cleaved crystal and a flexed crystal show excellent agreement with measured values. For the abraded crystal only the measured curve is shown because separate calculated curves are required for each dislocation density and the dislocation density increases rapidly toward the surface. From the data in Fig. 7 we conclude that it is feasible to adjust the diffraction efficiency of LiF over a considerable range and that calculations describe the efficiency accurately.

Figure 8 for KAP again shows excellent agreement between calculated and measured values even in the region of anomalous scattering near the potassium K absorption edge.

Figure 9 for seven different crystals demonstrates the large variation in efficiency for different practical crystals and the noticeable variation of efficiency with wavelength for many of the crystals.

From the work on crystal diffraction theory we conclude that it is practicable to predict response for any suggested new analyzer crystal, but more important, it is possible to predict the effect of crystal treatment (introduction of defects) designed to enhance the diffraction efficiency.

Fundamental parameters program (F.P.P.)

The fundamental-parameters method has always been recognized as requiring more elaborate mathematical calculations than the regression method. The reason for pursuing it was the important advantage of eliminating intermediate calibration standards which must otherwise be prepared for each range of composition and for each type of specimen. In 1965 when the 10-yr program started, Criss was already running a version of the fundamental parameters program on an IBM 1620 computer. His early program has been revised considerably to make it efficient in terms of cost and speed and to make it convenient for

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Table 1. Characteristic lines (1971)

<table>
<thead>
<tr>
<th>Line</th>
<th>Calculated</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr Ka</td>
<td>313</td>
<td>302</td>
</tr>
<tr>
<td>Cu Ka</td>
<td>202</td>
<td>215</td>
</tr>
<tr>
<td>Mo Ka</td>
<td>58</td>
<td>59</td>
</tr>
<tr>
<td>Rh Ka</td>
<td>32</td>
<td>31</td>
</tr>
<tr>
<td>La</td>
<td>51</td>
<td>56</td>
</tr>
<tr>
<td>W La</td>
<td>66</td>
<td>55</td>
</tr>
<tr>
<td>Au La</td>
<td>72</td>
<td>57</td>
</tr>
</tbody>
</table>

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Fig. 7. Calculated and measured X-ray diffraction efficiency for LiF crystal.

Fig. 8. Calculated and measured X-ray diffraction efficiency for KAP crystal.

Fig. 9. X-ray diffraction efficiency for common analyzer crystals.
using a selected error minimization function and whatever regression equation coefficients, \( a \), for all binary combinations of the intensities \( R_i \). Background and deadtime corrections can accordingly and prints out the weight per cent of the compounds.

(3) The analyst may fix the amount of any elements or compounds if they are known, as in the case of dilution or fusion.

(4) Absorption coefficients are calculated as needed from a three parameter fitting equation; this saves computer time as compared with looking for tabulated values in the memory bank.

(5) The cost of data treatment with complete interelement effects is less than 10c per element even in complex 10-15 component specimens.

The optimized approach in the current version of the program uses iteration to arrive at the best estimate of composition from the measured intensities. Some of the operation stages employ regression coefficients to approximate the intermediate estimates of composition. A summary of the sequences is as follows:

(1) Input measured X-ray intensities (as relative intensities \( R_i \)). Background and deadtime corrections can be automated if desired.

(2) The F.P.P. calculates a first estimate of regression coefficients, \( a_0 \), for all binary combinations of the elements in the specimen.

(3) A first estimate of composition is based on the regression equation

\[
C_j / R = 1 + \sum a_0 C_j
\]

using a selected error minimization function and whatever constraints are appropriate.

(4) The F.P.P. calculates new \( R_i \)'s from the first \( C_j \)'s using the full fundamental parameter equation.

(5) Disagreement between \( R_i \)'s and measured \( R_i \)'s is used to calculate a new set of \( a_0 \)'s.

(6) A second estimate of \( C_j \)'s is based on \( C_j / R = 1 + \sum a_0 C_j \).

(7) Iterate from step 3 until differences between successive sets of \( C_j \)'s are reduced to acceptable limits.

The current program has in it only two primary spectral standards for Fe and Ni base alloys. Three typical sets of results are shown in Table 2. Of the 14 elements present, 5 trace elements were held fixed and the remaining 9 elements were treated as variables in the fundamental-parameters program. Except for a slight bias of 1-2% relative for Ni all other components of 0.1% concentration or greater show satisfactory agreement. The relative errors in P or S are possibly caused by nonhomogeneous distribution of those elements (if absolute concentration of S or P is of explicit interest the error minimization function can be programmed to give them more importance). We believe the fundamental-parameters program has finally become a practicable approach for quantitative analysis and that the advantage of no intermediate standards should make it attractive for a wide variety of applications.

### Table 2. 1975 Results using fundamental parameters program

<table>
<thead>
<tr>
<th>Element</th>
<th>NBS 1151</th>
<th>NBS 1156</th>
<th>NBS 1160</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBS</td>
<td>X-Ray</td>
<td>NBS</td>
<td>X-Ray</td>
</tr>
<tr>
<td>Fe</td>
<td>67.17</td>
<td>67.18</td>
<td>69.90</td>
</tr>
<tr>
<td>Ni</td>
<td>7.07</td>
<td>6.93</td>
<td>19.0</td>
</tr>
<tr>
<td>Cr</td>
<td>22.13</td>
<td>22.11</td>
<td>0.20</td>
</tr>
<tr>
<td>Cu</td>
<td>0.25</td>
<td>0.25</td>
<td>0.03</td>
</tr>
<tr>
<td>Si</td>
<td>0.37</td>
<td>0.33</td>
<td>0.18</td>
</tr>
<tr>
<td>Mo</td>
<td>0.76</td>
<td>0.72</td>
<td>3.10</td>
</tr>
<tr>
<td>P</td>
<td>0.011</td>
<td>0.008</td>
<td>0.01</td>
</tr>
<tr>
<td>Mn</td>
<td>2.17</td>
<td>2.35</td>
<td>0.21</td>
</tr>
<tr>
<td>S</td>
<td>0.004</td>
<td>0.034</td>
<td>0.012</td>
</tr>
</tbody>
</table>

When we began the 10-yr program Criss was hopeful that it would be possible to program general matrix absorption and secondary fluorescence for heterogeneous specimens. He has been able to program the absorption part but secondary fluorescence is too complex to be practical except for a few oversimplified situations. Therefore we have abandoned the secondary fluorescence part. Using the absorption part alone it is possible to gain much valuable information about particle size effects even for specimens which have strong secondary fluorescence. For instance, the computer program can calculate the change in \( R \) for different particle sizes chosen by the analyst. This allows him to select the minimum amount of grinding which will give acceptable accuracy.

An example for Crescent ore is shown in Fig. 10. Actually Crescent ore is a Ag ore but the Ag has been neglected in the example because its small concentration does not change the nature of the variations in \( R_{Fe} \) with particle size. The most interesting result which can be seen from the curve is that the rate of change in \( R_{Fe} \) with particle size is much less for larger particle size than for small particle size. That is, the change in \( R_{Fe} \) between 150 mesh and 170 mesh size is only 0.6% relative but between 325 mesh and 400 mesh the change in \( R_{Fe} \) is 2.3% relative. The startling conclusion is that for this material the analyst will get much better results by not grinding below 170 mesh size. This is contrary to the accepted procedure of grinding mineral samples to 300 mesh or finer.

The point to be emphasized about bulk heterogeneous...
material is that one can calculate particle size effects quickly and economically and decide upon the optimum approach. Our experience of NRL is that the analyst cannot properly make such decisions based on intuition. In the example above the analyst would get extremely poor results by following the generally accepted procedure (i.e. that fine grinding is better than coarse grinding). In addition to getting better analysis from coarse grinding the cost of sample preparation would be reduced considerably.

Perhaps the most pressing need for particle size correction is not for bulk specimens which can be fused in borax is necessary but in pollution analysis where there is not enough material for fusion. For pollution specimens or other micro samples there is no need for secondary fluorescence correction and the particle size corrections can be used directly for quantitative analysis. Figure 11 shows the general particle size curve for micro samples.21 The abscissa is the product of size and the sum of linear absorption coefficients for incident and fluorescent radiation. The intensity is normalized to what would be obtained for infinitely small particle size. It is interesting that the size effect is quite similar for 5 μm particles of several metals and compounds as indicated.

One cannot use the curve of Fig. 11 in a practical way for analyzing unknown specimens because the composition must be known in order to know the linear absorption coefficient. Criss has found a practical way around the difficulty; he has used his computer program to calculate specific particle size effects for thousands of compounds and for both Cr and W primary radiation.23 From those calculations and by simplifying the particle size formulas he is able to express the equation

\[ \frac{I_i}{M_i} = S_i (1 + ab)^2 \]

where \( I_i \) is the measured intensity; \( M_i \) is the mass (this is desired parameter in the analysis); \( S_i \) is the sensitivity for element \( i \) (\( S_i \) must have been determined experimentally at some time for a sample of element \( i \) of small particle size); \( a \) is the particle size (known from collection conditions) \( b \) is the correction parameter which has been calculated for most common compounds. A few selected values of \( b \) taken from Criss' publication are shown in Table 3. The range of \( b \) values for Pb compounds is only a factor of 2 but for \( S \) compounds it is nearly a factor of 10.

For pollution analysis where the compounds are not known the accuracy would be limited by the extreme values of \( b \). Table 4 for 2 μm particles shows the variation in the correction term \((1 + ab)^2\) for compounds of 4 different elements. What the numbers in Table 4 tell us is that for Pb or Zn compounds the maximum error caused by not knowing the compound would be 10% but for \( S \) compounds it would be 40% and for Cl compounds 30%. There are maximum possible errors and can generally be improved by judicious use of other information about the specimen (for instance if no Pb is found in the specimen then the \( S \) correction cannot be as large as for PbSO₄).

Table 3. For W target X-ray tube 45 kV

<table>
<thead>
<tr>
<th>Pb compound</th>
<th>( b ) value</th>
<th>( S ) compound</th>
<th>( b ) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb O</td>
<td>0.030</td>
<td>(NH₄)₂SO₄</td>
<td>0.010</td>
</tr>
<tr>
<td>Pb S</td>
<td>0.023</td>
<td>Fe₃(SO₄)₂</td>
<td>0.033</td>
</tr>
<tr>
<td>Pb Br₂</td>
<td>0.018</td>
<td>ZnSO₄</td>
<td>0.050</td>
</tr>
<tr>
<td>Pb SO₄</td>
<td>0.015</td>
<td>PbSO₄</td>
<td>0.091</td>
</tr>
</tbody>
</table>

Table 4. Correction factor

\((1 + ab)^2\) for 2 μm particle size, W target

<table>
<thead>
<tr>
<th></th>
<th>Pb compound</th>
<th>( S ) compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn as metal:</td>
<td>((1 + 2 \times 0.026)^2 = 1.11)</td>
<td>((1 + 2 \times 0.007)^2 = 1.03)</td>
</tr>
<tr>
<td>Zn as ZnSO₄:</td>
<td>((1 + 2 \times 0.071)^2 = 1.40)</td>
<td>((1 + 2 \times 0.017)^2 = 1.07)</td>
</tr>
<tr>
<td>Pb in PbO:</td>
<td>((1 + 2 \times 0.030)^2 = 1.12)</td>
<td>((1 + 2 \times 0.091)^2 = 1.40)</td>
</tr>
<tr>
<td>Pb in PbSO₄:</td>
<td>((1 + 2 \times 0.015)^2 = 1.06)</td>
<td>((1 + 2 \times 0.017)^2 = 1.07)</td>
</tr>
<tr>
<td>S in (NH₄)₂SO₄:</td>
<td>((1 + 2 \times 0.017)^2 = 1.07)</td>
<td>((1 + 2 \times 0.091)^2 = 1.40)</td>
</tr>
<tr>
<td>S in PbSO₄:</td>
<td>((1 + 2 \times 0.010)^2 = 1.04)</td>
<td>((1 + 2 \times 0.091)^2 = 1.40)</td>
</tr>
</tbody>
</table>

**WHERE WE STAND TODAY**

During the 10 yr while the NRL program on data acquisition and interpretation was being carried out there was considerable progress in other areas of X-ray analysis as well. The solid state Si(Li) detector came into being and allowed energy dispersion to become a practical approach in both X-ray fluorescence and electron probe analysis. Interest in air and water pollution has helped push the limit of detectability by X-ray analysis down to the nanogram region. Solid state electronics have made it possible to build multiple-spectrometer X-ray instruments of reasonable size and competitive cost.

Table 5 summarizes the present capability for quantitative analysis of bulk specimens. For each of the 4 methods of exciting the X-ray spectrum the applicability of wavelength and energy dispersion is considered separately. The term trace constituent is used here to mean ppm level. Only X-ray tube excitation and wavelength dispersion allows quantitative measurements at trace levels in bulk specimens. In the analysis of minor constituents it is interesting to note that for electron excitation, wavelength dispersion is superior to energy dispersion because the peak/background ratio is better, but for positive ion excitation energy dispersion is

Table 5. Quantitative analysis of bulk samples

<table>
<thead>
<tr>
<th>Excitation</th>
<th>Dispersion</th>
<th>Major constituents</th>
<th>Minor constituents</th>
<th>Trace constituents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photon</td>
<td>A</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>E</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electron</td>
<td>A</td>
<td>X</td>
<td>X</td>
<td>?</td>
</tr>
<tr>
<td>+ Ion</td>
<td>A</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isotope</td>
<td>A</td>
<td>E</td>
<td>X</td>
<td>?</td>
</tr>
</tbody>
</table>
superior because the total intensity is too small to measure with a crystal spectrometer. With isotope excitation there is seldom enough intensity for wavelength dispersion even for major constituents.

Table 6 summarizes the present day capabilities for micro samples (1 mg is used as a representative quantity). None of the techniques is routinely quantitative for 1 ppm in 1 mg specimens although proton excitation can easily detect 1 ng of many elements and X-ray fluorescence can detect 1 ng of some elements. The only real differences between analyzing bulk specimens and analyzing micro specimens is one of the counting-rate available and in some instances the peak/background ratio.

Another item of concern in any method of analysis is the cost. Table 7 shows our estimates of 1975 costs for three different kinds of X-ray instruments. For laboratories doing less than 20 samples per day the sequential spectrometer is probably the most versatile instrument and can be operated either manually or automatically. The cost shown in Table 7 are for an automated instrument and show a cost of 75¢ per element or a cost of $11.00 per sample for 14 elements. If the number of samples per day goes up to 100 the sequential spectrometer cannot handle that many specimens and the energy dispersion instrument becomes more efficient. For 100 samples per day the cost is reduced to 25¢ per element. Finally if 200 samples per day are to be analyzed the most efficient instrument is the multiple-crystal-spectrometer equipment which reduces the cost to 17¢ per element. All of the above cost estimates include the appropriate kind of data interpretation. There will certainly be some disagreement with the costs shown and for some kinds of specimens they may be quite inaccurate; they are intended mainly as estimates so that other kinds of analysts may compare costs with their own techniques.

**THE FUTURE**

Speculation about what will happen in the future is always interesting to do but one should not be surprised or disappointed if such speculations are not very accurate. With this caveat stated let us consider some of the possibilities which will influence X-ray analysis in the future.

**Near future**

In the near future the use of multielectrode, pulsed X-ray tubes should become practical based on concepts already introduced by Goulding and Jaklovic. Figure 12 shows their cathode–anode arrangement with a control grid which can turn the tube off within 200 nsec after an X-ray photon has been detected. For energy dispersion applications this prevents pulse pile-up in the detector while a previous pulse is being processed. Allowed counting rate is increased from about 10,000 to over 20,000 counts/sec.

Valence effects in X-ray spectra (which have been known for over 50 yr) may become of practical interest especially for elements such as sulfur in pollution analysis. To test out the possibilities for micro samples we recently measured 50 μg/cm² samples of three sulfur compounds on a standard X-ray spectrometer. Figure 13 shows the same variations in S Kβ line structure which has been observed by other workers using more elaborate spectrometers and larger quantities of materials. From Fig. 13 it would seem to be feasible to distinguish the sulfide sulfur from the sulfate (or sulfite) forms and at the concentration of interest in pollution analysis. Of course the valence measurements must be made by wavelength dispersion because the resolution of the solid state detector is not adequate for the fine details.

![Fig. 12. Cathode-anode geometry for pulsed X-ray tube (Goulding and Jaklevic 1974).](image-url)
A third possibility for the near future is the increased use of time sharing on large (external or internal) computers to replace small dedicated computers attached to the X-ray equipment. The user appeal of small computers is unquestionable but the fact remains that only the large computers can carry out the more elaborate data interpretations in reasonable time. The cost and convenience of a teletype terminal to a large computer is competitive with the cost and convenience of a dedicated computer. It seems likely that much of the X-ray equipment operation function which has been used as an excuse for attached dedicated computers will soon be obtainable with even smaller programmable calculators; thus, to this author the need for dedicated computers is a questionable one.

More distant future

There are several areas where the concepts exist for dramatic advances in instrumentation and technique but we do not know how to achieve them as yet.

One such area is an improvement in energy resolution of gas proportional detectors. Gas detectors have the very important advantage over solid-state detectors in that they can discriminate against hard X-rays; thus they are much more useful in measuring low Z elements in the presence of high Z elements. The practical problem for gas detectors has been their poor energy resolution. However, we know that the expression used to describe the resolution, $\Gamma$, is incorrect.

$$\Gamma = 2.4\sqrt{(1.7\text{eV})}$$

where $\epsilon$ is the ionization potential (15.8 eV for Argon) and E is photon energy. This equation makes it appear that the resolution is limited theoretically by statistical uncertainty in the number of ion-electron pairs formed when an X-ray photon is absorbed. In reality it is the variation in electrons per avalanche which occurs in the internal amplification process which limits the resolution and does not obey the same random statistics. Perhaps reducing the internal gain in the detector and increasing the gain in a low-noise preamplifier would improve the gas detector resolution considerably.

X-ray lasers have been the subject of speculation for several years and may come into existence in the next decade. Their applications will be many but one simple use in X-ray analysis might be in situ air pollution analysis. The concentrations of interest are in the ng/cm$^3$ range which corresponds to ppm and should be measurable with a high intensity X-ray laser source.

The biomedical field is an area where instrumentation and techniques as well as concepts exist and yet the X-ray applications have never been as extensive as would seem possible and desirable. Perhaps the increased concern with health and the need to know the distribution of harmful elements within the various organs in the body may hasten such applications. How, for instance, can one say what the effects of pollution are unless he can measure the presence and variation of trace elements in biological material? Better specimen preparation and spectrometer geometry should improve the limit of detection to a usable range for medical interpretation.

SUMMARY

As we look back over the 60 yr existence of X-ray spectroscopy one of the most striking observations is the unusual and extreme contrasts. Periods of brilliant advances were interspersed with periods of appalling lethargy. The simplest concepts of any field of spectroscopy are combined with the most elaborate mathematical methods for quantitative data interpretation. The instrumentation is the most expensive but the costs per element for quantitative analysis are the lowest. The great advances in capabilities have not come from chemistry but from electronics (solid-state detectors, integrated circuitry, high-speed computers). Perhaps it is this very contrast which makes the field so fascinating and makes contemplation of what is 'over the horizon' in the future so exciting.

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