

## HIGH ENERGY ELECTRON IMPACT IONIZATION FOR ELEMENTAL ANALYSIS BY ENERGY DISPERSIVE X-RAY SPECTROMETRY

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A method has been demonstrated in which the emission of characteristic X-rays following impact ionization by electrons of several MeV energy is used for quantitative elemental analysis. Because of the unique properties of MeV electrons with respect to their X-ray production yield and range in solids, the method has comparable sensitivity over a wide range of elements and relatively less stringent sample preparation requirements. By using energy dispersive techniques to detect the X-rays, a simultaneous determination of the weight fraction of the elements in an unknown sample is possible from a procedure based entirely on empirically determined relative X-ray yields. The method was tested by analyzing three standard metal alloy samples obtained from the National Bureau of Standards. Elements ranging from iron ( $Z=26$ ) to lead ( $Z=82$ ) with concentrations from 0.06% to 88% were quantitatively determined. In general, good approximate agreement was found with the reported assays even for the minor constituents.

### Introduction

The intent of this study is to demonstrate the use and capability of 2 MeV electron impact ionization for elemental analysis by energy dispersive X-ray spectrometry. High energy electron impact ionization has some distinct advantages over other excitation methods. These advantages are characterized by the large range of MeV electrons in solids with a consequent small energy loss in thin samples, and by the smooth variation of the K-shell ionization cross sections with both atomic number and electron energy.<sup>1</sup> The X-ray production from photon excitation methods (X-ray tubes and radioactive sources) can vary rapidly from element to element because of the atomic shell structure effects. For this reason, several X-ray target tubes or several radioactive sources are usually required to cover the entire periodic range of elements<sup>2</sup>. In contrast to using photon sources, the production yield of X-rays by several MeV electron impact ionization is comparable over the entire range of elements. For example, the K X-ray production cross-section for 2 MeV electron impact, as reflected by the product of the K-shell ionization cross-section<sup>1</sup> and the fluorescence yield,<sup>3</sup>

varies smoothly and gradually from  $\sim 55$  barns at calcium ( $Z = 20$ ) to a maximum of  $\sim 65$  barns at nickel ( $Z = 28$ ) and decreases to  $\sim 10$  barns at lead ( $Z = 82$ ). An additional feature of the ionization cross sections at several MeV is that even for a change in incident electron energy by several percent, the difference in X-ray production yield is negligible. Compared to the electron microprobe<sup>4</sup> or the more recently explored technique of ionization by positive ion impact,<sup>5</sup> high energy electrons enjoy the advantage of a far smaller energy loss per unit length in solid materials. Therefore, the limitations of target preparation are relatively minor, and the general problems of matching unknown and reference sample matrices are less severe. The large range for high energy electrons and their relatively constant (with energy) ionization cross-section makes the X-ray production intensity approximately uniform throughout the electron path length in the target. Thus, the entire target thickness is sampled with the same X-ray production efficiency. This is in contrast to the situation for the electron microprobe or positive ion excitation, where iterative approximations are necessary to calculate the X-ray production as a function of the depth of the interaction in the target.<sup>6</sup>

Interfering background radiation is not unique to any of the specific extraction methods. Like the electron microprobe, high energy electron impact ionization is limited by the background interference due to electron bremsstrahlung produced in the target. Although bremsstrahlung production is inherently small for positive ions, these projectiles give rise to knock-on electrons, which in turn produce bremsstrahlung. Even with the X-ray sources, there is a continuous background due to incoherent Compton scattering of the exciting radiation.

For these studies, a simple and rapid method was developed which is based entirely on empirically determined relative X-ray yields. No sample matrix corrections (cf. Gould and Bates<sup>7</sup>) were used in the method to show that excellent approximate quantitative determinations can be obtained without the corrections. It must be realized of course, that all of the sophisticated corrections which apply to other X-ray methods can also be implemented in this method.

Three standard samples of metal alloys were used to test the method over a wide range of elements and concentrations. They are cast bronze (NBS No. 52), a tin-base bearing metal (NBS No. 54), and a phosphor bronze metal (NBS No. 63) obtained from the National Bureau of Standards.

### Methodology

Quantitative elemental analysis by X-ray spectrometry is effected by relating measured X-ray intensities to the amount of an element in a sample. The simplest approach is to establish the proportionality constant for the relation with pure elements, and then use this constant to determine the amount of the element in an unknown sample. This method, of course, neglects all sample matrix effects which enhance or reduce the X-ray production and which attenuate the X-ray emission intensity. In addi-

tion, it requires the normalization of two measurements, i. e. the X-ray intensity for the pure element and that for the same element in the unknown sample. Another possible approach that is frequently used employs comparison standards which closely resemble the unknown sample. This attempts to account for the deviations from proportionality due to matrix effects but requires the difficult contrivance of a comparison standard for each unknown or type of unknown sample. Again, the two measurements for the standards and the unknown must be normalized before a comparison can be made.

The procedure adopted for this study incorporates in spirit the major features of both the above methods, and in addition has one further advantage. Like the first method, it attempts to establish a constant of proportionality between the amount of an element and its X-ray intensity. This is accomplished by determining relative X-ray yields for all the elements with respect to that for a primary reference element. The relative yields are obtained by simultaneously measuring the X-ray intensities for the primary reference and another element in a reference sample containing a known relative amount of both. In this way, the X-ray yields for all the elements are determined with respect to each other. Using these relative yields, relative amounts of the elements in an unknown sample can then be determined from their measured X-ray intensities which are simultaneously obtained from the spectrum of the unknown sample. Similarly, the fraction of a given element in the total amount of unknown sample material can be determined from the relative yield adding a known relative amount of an internal reference element to the unknown sample.

A first order approximation to the comparison standard method is used to eliminate deviations in the yields because of matrix effects. The approach is to get all the unknown and reference samples to resemble each other. This is, of course, impossible in the strictest sense, but in the limit of relatively uniform and thin samples, an adequate approximation should be attainable. The procedure used here to obtain approximately similar targets for the electron irradiation consists of dissolving the solid samples and absorbing the solutions onto identical thin absorbent supporting matrices. Due to the unique properties of high energy electrons with respect to range and ionization characteristics, as discussed in the Introduction, the X-ray production is essentially constant throughout the target thickness. Thus, no corrections for matrix effects are necessary for the primary excitation process. X-ray production from secondary fluorescence and by bremsstrahlung generated in the target contributes at most a few percent for targets that are only a few  $\text{mg}/\text{cm}^2$  thick. Depending on the sample composition, self-absorption in the target can be an important effect. Still, because of the target preparation method used, the latter two matrix effects are compensated to first order. Furthermore, they can be more easily taken into account because no corrections are necessary for the primary excitation process.

The additional advantage of this procedure is that it does not require the absolute comparison of two or more measurements. This results from the fact that all

of the measurements are relative. For the same reason, it does not require any absolute measurements, such as for the amount of target material or the number of X-rays. Details of this analysis procedure follow.

### Relative yields

Reference samples, containing a known relative amount of primary reference element and one or two other elements, are used to establish the relative X-ray yields. The yields reflect not only the X-ray production (ionization cross section and fluorescence yield) but also the efficiency of observation for a particular target and detector configuration, and include the effects of geometry and absorption. Cadmium is used as the primary reference element with the Cd  $K_{\alpha}$  X-ray yield taken as unity. This definition is purely arbitrary since any other X-ray yield can be chosen as the standard. In each spectrum, obtained from electron irradiation of the reference targets, the number of X-rays in each X-ray line is measured relative to the yield of the Cd  $K_{\alpha}$  X-ray. That is, the relative yield for the  $\eta$  X-ray of element Z is

$$Y_{\eta}(Z) = \frac{N_{\eta}(Z)}{N_{K_{\alpha}}(Cd)} \cdot \frac{a_{Cd}}{a_Z} \quad (1)$$

where  $N_{\eta}(Z)$  - measured number of  $\eta$  X-rays from element Z,

$N_{K_{\alpha}}(Cd)$  - measured number of Cd  $K_{\alpha}$  X-rays,

$a_Z/a_{Cd}$  - known atom ratio of element Z to Cd.

These yields refer not only to a particular element Z, but also to a particular X-ray line. The relative yields can also be measured with respect to a secondary reference element once its relative yield with respect to the Cd  $K_{\alpha}$  yield is established. When the yields are measured with respect to a secondary reference, they are still expressed on a basis respect to the primary reference yield. The important consequence of this is that the yields of all the elements are determined relative to each other.

### Elemental analysis

A detection system is essentially calibrated for quantitative elemental analysis once the relative yields are measured. The method is well suited for the simultaneous assay for many constituent elements in an unknown since its X-ray spectrum contains the detectable K and L X-rays for all the elements present in the sample. Relative amounts of each constituent element are determined from the measured X-

ray intensities in the spectrum and their relative yields. To illustrate, the weight fraction of element A with respect to element B in an unknown sample is

$$\frac{m_A}{m_B} = \frac{N_\mu(A)}{N_\nu(B)} \cdot \frac{W_A}{W_B} \cdot \frac{Y_\nu(B)}{Y_\mu(A)} \quad (2)$$

where  $N_\mu(A)/N_\nu(B)$  - ratio of the measured number of  $\mu$  X-rays from element A to the number of  $\nu$  X-rays from element B obtained from the same spectrum,

$Y_\mu(A)$ ,  $Y_\nu(B)$  - refer to the respective relative yields [Eq. (1)] for  $\mu$  X-ray of element A and  $\nu$  X-ray of element B,

$W_A/W_B$  - atomic weight ratio to convert the relative yields from an atom to mass basis.

Not all the elements in a sample are necessarily observed due to detection limitations. Therefore, the single measurement described above will not account for the total amount of sample unless all of the constituent elements are detected. With unknown samples, this condition is never known with certainty, and an additional measurement is necessary to obtain the true percentage of the element in the unknown. This second measurement is made with a known relative amount of an internal reference element added to the sample. For a sample containing a known ratio, ( $m_{\text{total}}/m_Z$ ), of unknown sample weight  $m_{\text{total}}$  to reference element Z weight,  $m_Z$ , the weight fraction of element A in the unknown, ( $m_A/m_{\text{total}}$ ) is obtained from:

$$\frac{m_A}{m_{\text{total}}} = \frac{N_\mu(A)}{N_\eta(Z)} \cdot \frac{W_A}{W_Z} \cdot \frac{Y_\eta(Z)}{Y_\mu(A)} \cdot \frac{m_Z}{m_{\text{total}}} \quad (3)$$

where  $N_\mu(A)/N_\eta(Z)$  - ratio of the measured number of  $\mu$  X-rays for element A to the  $\eta$  X-rays for reference element Z,

$Y_\eta(Z)$ ,  $Y_\mu(A)$ ;

$W_A/W_Z$  - are given as before.

This entire procedure for measuring the relative yields and making elemental assays, as outlined in Eq. (1) through (3), requires only relative measurements. All of the measured quantities are obtained from ratios of simultaneously recorded X-ray intensities and weight ratios. It, therefore, does not require any absolute measurements of the number of atoms or the number of X-rays processed. Neither is it necessary to know the efficiency of the X-ray detection device.

## Experimental

### Electron source

Electrons were accelerated to 2.04 MeV with the 4 MeV Dynamitron Accelerator at the State University of the New York at Albany. The accelerated electron beam, directed along an evacuated beam line, was centered at the target position by electrostatic and magnetic steering. The experimental section of the beam line consisted of: (a) the target chamber fabricated from a 10 cm diameter beam tube cross; (b) a 2.5 m long 10 cm diameter beam pipe downstream from the target chamber serving both as a beam dump and as a connecting pipe to a vacuum station; (c) a 1 cm diameter removable aperture located 30 cm upstream from the target chamber; (d) a vacuum gate valva used to close off the accelerator vacuum when opening the target chamber to air for target changes; and (e) a high speed molecular diffusion vacuum pump and a roughing pump used to re-evacuate the target chamber. The aperture, target chamber and beam dump were electrically insulated from each other and the remainder of the beam line. Current measurements on them allowed the electron beam to be located, positioned and monitored.

### Target preparation

The general procedure used to prepare a target for electron irradiation and the subsequent X-ray measurements consisted of immersing a thin absorbent lens tissue into a sample solution, air drying and mounting on an aluminium target frame. The lens tissues were Fisher No. 11-996 which have a thickness of approximately 1.35 mg/cm<sup>2</sup>. Sample solutions were prepared by dissolving a given sample in an appropriate solvent. Reference samples for elements from chromium (Z=24) to bismuth (Z=83) were prepared by weighing out known relative amounts of element Z and cadmium. Both pure elements and compounds containing the elements were used for the reference samples. In general, the starting sample materials were of reagent grade quality. The reference solutions were prepared using ~10 mmoles of each element and made to about 0.5 M in an aqueous acidic medium. Several were made by dissolving soluble compounds of the elements in water. Solutions of material elements or water insoluble compounds were usually made using a minimum amount of concentrated HCl or HNO<sub>3</sub> and then were diluted. Knowledge of the actual solution concentration is not necessary since only the ratio of the number of atoms of each element is important. The Z/Cd atom ratios for all both the heaviest (Z ≥ 60) elements were around unity. For the heavier elements, the Z/Cd atom ratio was ~2. The complete dissolution of the weighed sample in the chosen solvent is the most critical requirement for the target preparation. If either or both of the two elements or compounds do not completely dissolve in the solvent, then the atom ratio on the target will be in error. Fortunately, the lens tissues were sufficiently durable to with-

stand even concentrated nitric acid or aqua regia. This added considerable flexibility in the choice of solvents.

The NBS standards were dissolved in aqua regia for use as unknown sample solutions. After taking up in a minimum volume of acid, the solutions were boiled and agitated to expel  $\text{NO}_2$ , and diluted to 10-30 mg/ml. Lens tissue targets of the standards with a known relative amount of cadmium were also prepared by accurately weighing out amounts of the standard and cadmium metal. These samples were also dissolved in aqua regia to concentrations of 60-120 mg/ml. The known ratios of unknown sample weight to reference Cd weight  $m_{\text{total}}/m_{\text{Cd}}$  were of the order of 0.5-1.0. Although it need not be known for any of the analyses, it was found that the total amount of sample material on a target is typically 1-2 mg/cm<sup>2</sup>. This represents about  $10^{18}$  atoms/cm<sup>2</sup> for each reference element in the targets. atoms/cm for each reference element in the targets.

### X-ray spectrometers

The X-ray spectra were obtained with liquid nitrogen cooled lithium drifted silicon and germanium detectors. According to the manufacturers specifications, the Si(Li) detector (Princeton Gamma Tech LS23) had a 4 mm diameter x 3 mm deep active region, and the Ge(Li) detector (Ortec GX-299B) had a 6 mm diameter x 4.79 mm deep active region. The Si(Li) detector had a 7 mm diameter x 0.025 mm thick Be entrance window, while the Ge(Li) detector had a 0.127 mm Be window and a  $40.4 \mu\text{g}/\text{cm}^2$  gold layer evaporated onto its front face. Both detectors were coupled to charge sensitive FET preamplifiers [Princeton Gamma Tech RS-10 for the Si(Li) and Ortec 118A for Ge(Li) detector]. Pulses from the preamplifiers were amplified (Ortec 452) and analyzed with a 4096 channel 50 MHz ADC (Northern Scientific NS-625) interfaced to a PDP-15 on-line computer. The on-line computer served as both the memory device for the spectrometers and for simple data reduction.

For measurements with the Ge(Li) detector, the target chamber was fitted with a 2.54 cm diameter x 0.051 mm thick Mylar window. This X-ray exit window was located at 10.2 cm from the target centre. The Ge(Li) detector was located at a distance of 38.6 cm from the exit window. Thus, the path for an X-ray from the centre of the target to the detector consisted of 10.2 cm vacuum, 0.051 mm Mylar, 38.6 cm air, 0.127 mm Be, and  $40.4 \mu\text{g}/\text{cm}^2$  Au. The Si(Li) detector was directly vacuum coupled to the target chamber and was located at a distance of 51.5 cm from the target centre. The only absorbing layer in the X-ray path was the Be entrance window on the detector. The detector was connected to the target chamber through a vacuum gate valve which was used to keep the region in front of the entrance window evacuated during target changing. In each system, the detector was located at  $90^\circ$  with respect to the incident electron beam direction. All surfaces visible to the detector were covered by a graded Cu-Al-plastic absorber to shield out fluorescent X-rays from surrounding materials. A 1000 gauss sweeping magnet was used to sweep

scattered electrons away from the front of the entrance windows and prevent them from entering the detectors. The magnet was molded into a plastic cast with a 4 cm hole between the pole pieces. The purposes of the plastic cast was to present the swept electrons with a light element material, instead of allowing them to interact with the heavier element metals of the magnet which would produce a higher bremsstrahlung and X-ray background. The entire setup, including the cryostat, was further shielded with a minimum of 5-10 cm of lead against background radiation from the beam dump.

### Measurement procedures

The electron beam, accelerated to  $2.4 \pm 0.01$  MeV for these studies, was steered by electrostatic and magnetic deflection through the 1 cm diameter aperture. Once the electron beam was positioned, the aperture was removed before starting the measurements. The target, mounted on an aluminium frame, was placed in the target chamber at  $45^\circ$  to the incident electron beam direction. During each run, the electron beam was monitored by current measurements. The total current on the electrically insulated beam tube from the target chamber to the end of the beam dump was measured. Typically, the runs made with the Ge(Li) detector were of 5-15 min duration with electron currents of 25-50 nA for the reference targets, and 60-80 min at 50 nA for the unknown (NBS samples) targets. The spectra of the reference targets obtained with the Si(Li) detector were accumulated for 10-30 min at 25-50 nA for the reference targets, and approximately 180 min at 50 nA for the unknown targets.

The resultant spectrum obtained from a run contains the detectable K and L X-rays of all the elements present in the target. The range of X-rays that can be detected is limited by absorption for the low energy X-rays and by detection efficiency for the high energy X-rays. With the Si(Li) detector, the lightest detectable element was aluminium ( $Z = 13$ ). Quantitative yields were measured however, only for those elements above chromium ( $Z = 14$ ) where absorption was not too great and where the  $K_\alpha$  and  $K_\beta$  X-rays were easily resolved. Above ytterbium ( $Z = 70$ ), K X-ray yields were not measured with the Si(Li) detector because of the low detection efficiency at these high energies. The Ge(Li) detector was used mainly for measurements of the K X-ray yields for the heavy elements ( $Z = 47 - 83$ ). Typical spectra from reference targets obtained with the Si(Li) and Ge(Li) detectors are shown in Fig. 1 and 2, respectively. Most of the peaks in the spectra are not singlets, but rather are unresolved multiplets of closely lying X-ray lines. They were not resolved because of the finite detection resolution of the spectrometers which was typically 300-400 eV. Those multiplets which were not resolved, e. g. Cu K  $\alpha_1$  and K  $\alpha_2$  (see Fig. 1 curve a), were treated as single peaks. Doublets which were partially resolved were stripped into two single peaks. Spectrum stripping was not attempted for the higher order multiplets. Peak stripping of unresolved and partially resolved X-rays



from two or more different elements can be effected by using known yield ratios, e.g.  $Y_{K\beta}/Y_{K\alpha}$  ( $Z$ ) or by a curve fitting procedure using standard line shapes for single peaks. An example of the first case is shown in Fig. 1, Curve b) where the  $\text{Sn } K_{\alpha}$  and  $\text{Cd } K_{\beta}$  X-rays are not completely resolved. The  $\text{Sn } K_{\alpha}$  intensity can be determined, however, from the intensity of the  $\text{Cd } K_{\alpha}$  line and from

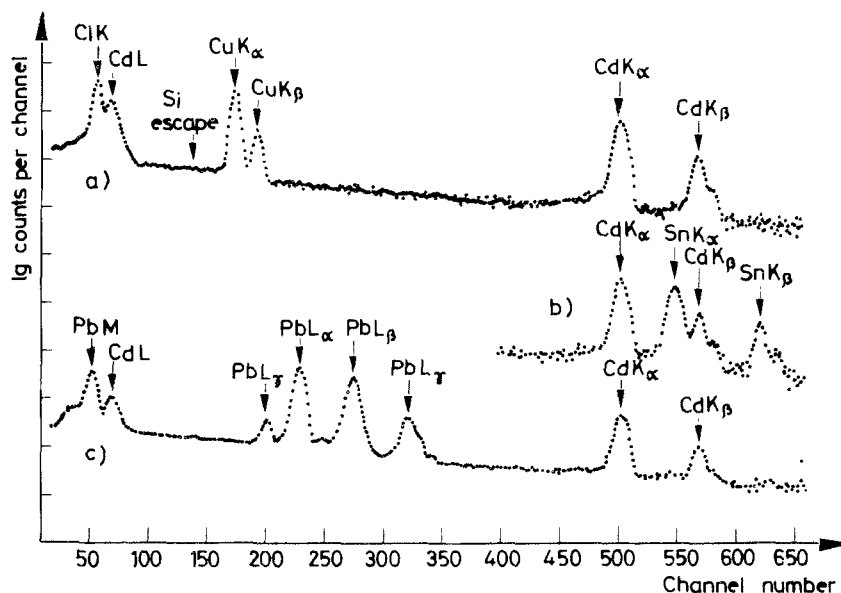


Fig. 1. Typical X-ray spectra of the reference samples obtained with the  $\text{Si(Li)}$  detector: Curve a -  $\text{Cu/Cd}$  (atom ratio: 1.0612) after 40 min run with 2 MeV electrons at 20 nA current; Curve b -  $\text{Sn/Cd}$  (atom ratio: 0.7761) after 14 min run with 2 MeV electrons at 50 nA current; Curve c -  $\text{Pb/Cd}$  (atom ratio: 2.0278) after 27 min run with 2 MeV electrons at 50 nA current

a priori knowledge of the  $Y_{K_{\alpha}}(\text{Cd})/Y_{K_{\alpha}}(\text{Cd})$  ratio. The ratio is obtained from another reference spectrum, such as  $\text{Cu/Cd}$  (Fig. 1 Curve a) or  $\text{Pb/Cd}$  (Fig. 1 Curve c), where the Cd X-rays are unmasked. This procedure is possible whenever at least one of the major X-ray lines of a pair of nearby elements is completely resolved. Fig. 2 contains an example of the second case. The unresolved Cd K and Ag K X-ray peaks in the  $\text{Ag/Cd}$  spectrum (Fig. 2 Curve b) can be stripped out by fitting the  $\text{Cd } K_{\alpha}$  and  $K_{\beta}$  X-ray line shapes from the  $\text{Br/Cd}$  spectrum (Fig. 2 Curve a) to the masked peaks.

The procedure used to determine the relative yields and to analyze for the various constituents in the NBS metal alloys has been outlined in the Methodology section.

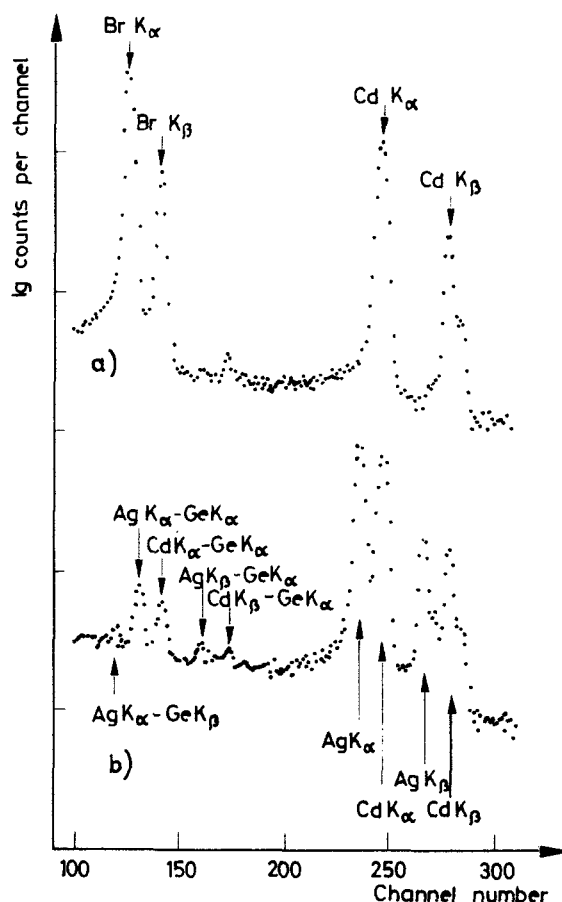


Fig. 2. Typical X-ray spectra of the reference samples obtained with the Ge(Li) detector: Curve a - Br/Cd (atom ratio: 2.0000) after 5 min run with 2 MeV electrons at 30 nA current; Curve b - Ag/Cd (atom ratio: 0.9754) after 2 min run with 2 MeV electrons at 45 nA current

Quantitative determination of an element can be made by analysis of any one of several of its X-rays provided the relative yield for this X-ray has been previously determined. This offers considerable flexibility in making the analyses. For example, the unfavorable Si(Li) detection efficiency for the K X-rays of very heavy elements can be circumvented by using their lower energy L X-rays for the analysis. For the assay of the NBS samples, the K X-rays were used exclusively, except with the Si(Li) detector in the case of the Pb determination where the L X-rays were used. The Ge(Li) detector was used only for the determination of elements above tin.

## Results and discussion

The relative  $K_\alpha$  and  $K_\beta$  X-ray yields,  $Y_{K_\alpha}(Z)$  and  $Y_{K_\beta}(Z)$  as measured with the Ge(Li) and the Si(Li) detectors are listed in Table 1. In principle, the yields obtained with either detector can be used for quantitative elemental analysis. Alternatively, the Si(Li) detector can be used for the lighter elements and the Ge(Li) detector for the heavier elements in order to have a comparable sensitivity for the entire range of elements from  $Z = 24$  to  $Z = 83$ . However, there are practical limitations which arise both from the inherent properties of the respective detectors and from the incidental differences in detector dimensions and constructional details. A discussion of the differences in the two detection systems and their resultant performance follows.

For low energy X-rays, the vacuum path and thin entrance window (0.025 mm Be) associated with the Si(Li) system was definitely favored over the air path and thicker windows (0.13 mm Be and 0.051 mm mylar) of the Ge(Li) system. The Ge(Li) detector, being larger in size and higher in intrinsic detection efficiency, should be more advantageous at high X-ray energies. These advantages are offset, however, by the occurrence in the spectrum of secondary peaks associated with the escape of a Ge X-ray from the detector. Fig. 2 Curve b illustrates this effect for the Ag/Cd reference sample. Each of the two K X-ray lines from Ag and Cd gives rise to two additional peaks corresponding to the escape of a Ge  $K_\alpha$  or  $K_\beta$  X-ray from the detector. Thus, even for this simple two element sample, eight escape peaks can result.

The presence of the escape peaks affects the spectral analysis in two ways. First, the escape peaks resulting from one element can underlie the full energy peaks of another element. An example of this is shown in Fig. 2 Curve a for the Br/Cd reference sample where the ( $\text{Cd } K_\alpha - \text{Ge } K_\alpha$ ) and ( $\text{Cd } K_\alpha - \text{Ge } K_\beta$ ) escape peaks are completely masked by the intense Br  $K_\alpha$  and  $K_\beta$  lines. In this situation, the intensity of the escape peaks for Cd must be measured and their values must be subtracted before an accurate value for the Br intensity can be obtained. Second, care must be exercised to avoid the misidentification of an escape peak as the characteristic X-ray of another element.

Although the escape peak phenomenon is also present in the Si(Li) detector (see e.g. Fig. 1 Curve a) it is of considerably less importance. This is a result of the low K X-ray fluorescence yield of 0.047 for Si as compared to the value of 0.540 for Ge.<sup>3</sup> Furthermore, because of its low energy, a Si K X-ray is less likely to escape from the corresponding detector than a Ge K X-ray. Compared with the Ge(Li) detector, the Si(Li) detector has the disadvantage of a lower detection efficiency for high X-ray energies. However, this can be circumvented by analysis of the heavy elements via their L X-ray lines. Thus, the Si(Li) detector appears to be in general the more useful the detector for elemental analysis.

Fig. 3 shows typical X-ray spectra for a phosphor bronze bearing metal (NBS No. 63) measured with the Ge(Li) and the Si(Li) detectors system. Weight ratios  $m_{\text{Sb}}/m_{\text{Sn}}$

Table 1

Relative K X-ray yields on an atom basis normalized to Cd  $K_{\alpha}$  yield of unity  
for the Ge(Li) and the Si(Li) detector system

Element	Atomic number Z	Ge(Li)		Si(Li)	
		$Y_{K_{\alpha}}(Z)$	$Y_{K_{\beta}}(Z)$	$Y_{K_{\alpha}}(Z)$	$Y_{K_{\beta}}(Z)$
Cr	24	—	—	2.821	0.376
Mn	25	—	—	3.196	0.431
Fe	26	—	—	3.403	0.457
Co	27	—	—	3.593	0.522
Ni	28	—	—	3.876	0.553
Cu	29	—	—	3.583	0.512
Zn	30	—	—	3.618	0.523
As	33	—	—	3.209	0.485
Se	34	—	—	2.818	0.434
Br	35	1.309	0.260	3.105	0.494
Rb	37	—	—	2.901	0.471
Sr	38	—	—	2.583	0.433
Ag	47	1.193	0.249	1.348	0.226
Cd	48	1.000	0.224	1.000	0.172
In	49	0.968	0.202	0.881	0.138
Sn	50	0.972	0.214	0.815	0.127
Sb	51	0.960	0.214	0.704	0.116
Te	52	0.870	0.199	0.610	0.0967
Ba	56	0.734	0.185	0.331	0.0579
La	57	—	—	0.192	0.0343
Ce	58	—	—	0.214	0.0369
Pr	59	—	—	0.198	0.0366
Nd	60	0.541	0.136	0.157	0.0248
Sm	62	0.534	0.135	0.127	0.0222
Eu	63	—	—	0.118	0.0219
Gd	64	0.524	0.135	0.107	0.0177
Er	68	0.451	0.111	0.0589	—
Yb	70	0.409	0.0978	0.0431	—
Pt	78	0.284	0.0678	—	—
Pb	82	0.223	0.0480	—	—
Bi	83	0.209	0.0432	—	—

and  $m_{Pb}/m_{Sn}$  determined from these and similar spectra for the other two NBS metal alloy samples are compared in Table 2 with values obtained from the reported assays. With the Ge(Li) detector, both Sb and Pb were determined relative to Sn by measurements of the  $K_{\alpha}$  X-ray intensities of the three elements in the same spectrum.

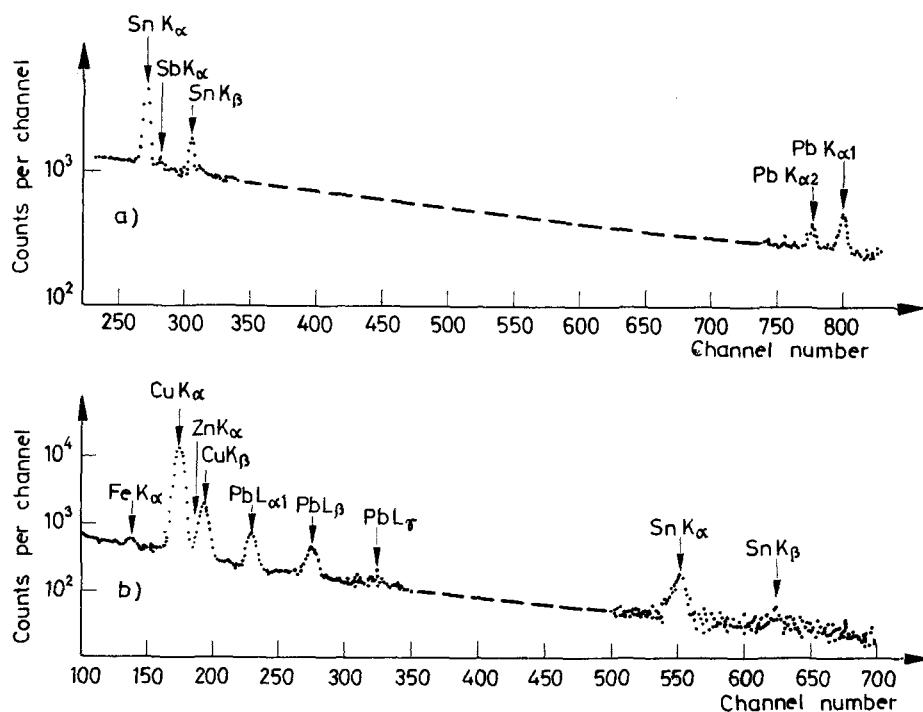


Fig. 3. Spectra of the phosphor bronze bearing metal (NBS No. 63): a - obtained with the Ge(Li) detector in a 58 min run with 2 MeV electrons at 50 nA current; b - obtained with the Si(Li) detector in a 17 min run with 2 MeV electrons at 85 nA current

The determinations with the Si(Li) detector were made using the  $Sn K_{\alpha}$  and  $Sb K_{\alpha}$  X-rays for the  $m_{Sb}/m_{Sn}$  weight ratio, and the  $Sn K_{\alpha}$  and the  $Pb L_{\alpha 1}$  and  $L_{\beta}$  X-ray lines for the  $m_{Pb}/m_{Sn}$  weight ratio. The relative yields for the two Pb L lines were obtained from the Pb/Cd reference sample (see Fig. 1 Curve c) in a similar manner to that used to obtain the relative K X-ray yields. They are, relative to the  $Cd K_{\alpha}$ , 4.221 for the  $Pb L_{\alpha}$  and 2.929 for the  $Pb L_{\beta}$ . As seen in Table 2, the results for the  $m_{Pb}/m_{Sn}$  analysis with the Si(Li) detector are more accurate than those obtained with the Ge(Li) detector. This is a result of the higher relative yield of the Pb L X-rays in the Si(Li) detector as compared to the relative yield

of the Pb K X-rays in the Ge(Li) detector which leads to a more favorable detection sensitivity for Pb with the Si(Li) detector. For the  $m_{\text{Sb}}/m_{\text{Sn}}$  determinations, little difference is expected between the results for the Ge(Li) and Si(Li) detectors since the relative yields for the Sb  $K_\alpha$  and Sn  $K_\alpha$  are almost identical for both detectors. The seeming superiority of the Ge(Li) detector over the Si(Li) detector for the case of NBS-63 is due principally to the better counting statistics in the spectrum

Table 2

Comparison of reported  $m_{\text{Sb}}/m_{\text{Sn}}$  and  $m_{\text{Pb}}/m_{\text{Sn}}$  weight ratios to experimental values obtained with the Ge(Li) and the Si(Li) detector system

Sample	$m_{\text{Sb}}/m_{\text{Sn}}$	$m_{\text{Pb}}/m_{\text{Sn}}$
NBS-52		
Reported	0.020	0.192
Found Ge(Li)	—	0.138
Found Si(Li)	—	0.210
NBS-54		
Reported	0.083	0.0063
Found Ge(Li)	0.083	—
Found Si(Li)	0.082	0.0061
NBS-63		
Reported	0.055	0.98
Found Ge(Li)	0.059	1.06
Found Si(Li)	—	1.02

obtained with the former. In the absence of clear evidence favoring the use of the Ge(Li) detector, only the data obtained with the Si(Li) system were used in the following complete assay of the three NBS samples.

A typical spectrum used for the analyses is shown in Fig. 4a. Since Cu was a major constituent of all three samples, weight ratios  $m_Z/m_{\text{Cu}}$  were determined through the use of Eq. (2) from the measured X-rays spectra. Except for the lead analysis which used the Pb  $L_\alpha$  and  $L_\alpha$  lines, the  $K_\alpha$  X-rays of each element were used for the determinations. In the iron analysis, a correction had to be made for the Si X-ray escape peak corresponding to the Cu  $K_\alpha$  line (Cu  $K_\alpha$  —  $K = 6.3$  keV) which was not resolved from the Fe  $K_\alpha$  X-ray (6.4 keV). Although the escape peak represents only a small fraction\* of the corresponding main peak, it is a signi-

\*The intensity ratio of the Si escape peak to the Cu  $K_\alpha$  full energy peak was separately measured to be  $(6.3 \pm 0.3) \cdot 10^{-3}$ .

ificant correction when there is a small amount of Fe in the presence of a large amount of Cu as it is the case for the samples studied.

The  $m_{\text{Cu}}/m_{\text{total}}$  weight ratios in the three NBS standards were determined from spectra of samples containing a known weight ratios,  $m_{\text{total}}/m_{\text{Cd}}$ , of the standard

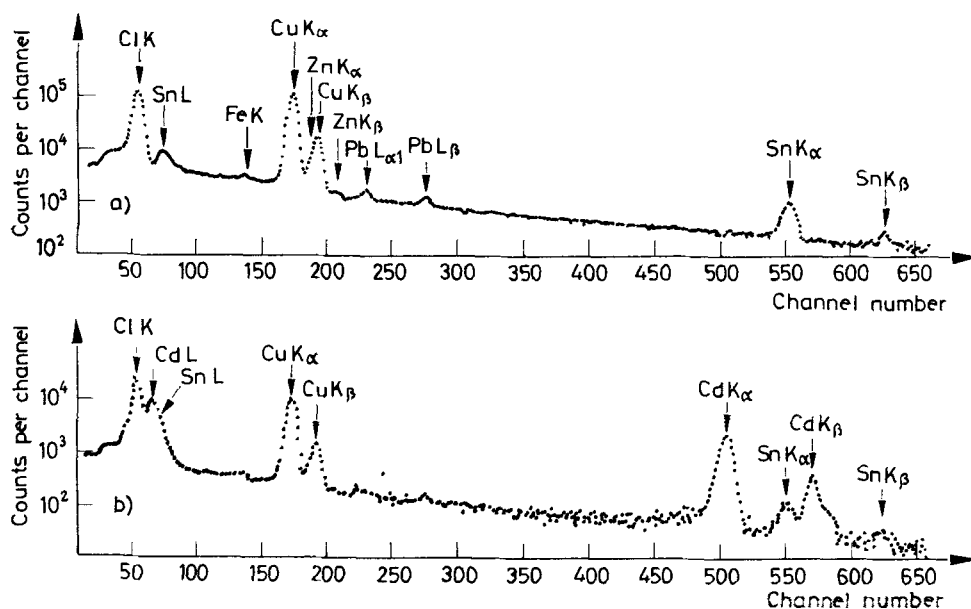


Fig. 4. Spectra of the cast bronze (NBS No. 52) obtained with the Si(Li) detector: a - in a 180 min run with 2 MeV electrons at 30 nA current; b - with added reference Cd (weight ratio: 0.5613) in a 27 min run with 2 MeV electrons at 25 nA current

to internal reference Cd weight. Fig. 4b shows such a spectrum for the cast bronze (NBS No. 52) sample. The weight ratios,  $m_{\text{Cu}}/m_{\text{total}}$ , were determined through the use of Eq. (3) from the measured intensities of the Cu  $K_{\alpha}$  and Cd  $K_{\alpha}$  X-rays in the same spectrum. The results are compared with the reported NBS assays in Table 3. The largest discrepancy between the experimental and the reported  $m_{\text{Cu}}/m_{\text{total}}$  weight ratio found for the three samples is 7%. The results for the  $m_{\text{Cu}}/m_{\text{total}}$  and the  $m_{\text{Z}}/m_{\text{Cu}}$  weight ratios can be combined to obtain the weight ratio  $m_{\text{Z}}/m_{\text{total}}$  of element Z in the sample. Thus, from the two sets of measurements, one can construct the percentage of each detected element in the total sample. The results are also listed in Table 3.

Table 3

Comparison of reported and measured assays for the NBS metal alloy samples in weight percent

Element	Atomic Number Z	NBS No. 52		NBS No. 54		NBS No. 63	
		Reported	Found	Reported	Found	Reported	Found
Al	13	—	—	—	—	0.05	—
P	15	—	—	—	—	0.62	—
S	16	—	—	—	—	0.06	—
Fe	26	0.12	0.17	0.06	0.07	0.27	0.31
Ni	28	0.13	—	—	—	0.008	—
Cu	29	88.33	91.78	3.75	3.77	78.05	83.21
Zn	30	1.89	1.68	—	—	0.48	0.51
As	33	—	—	0.05	—	0.19	—
Sn	50	7.90	8.05	88.24	85.77	9.91	9.96
Sb	51	0.16	—	7.33	7.05	0.55	—
Pb	82	1.52	1.70	0.56	0.52	9.74	10.18
Bi	83	—	—	0.05	—	—	—

### Conclusions

In the experimental analyses of the NBS samples a quantitative determination of elements ranging from iron ( $Z = 16$ ) to lead ( $Z = 82$ ) and with the concentrations ranging from 0.06% to 88% was performed. In general, good approximate agreement was found with the reported assays even for the minor constituents. Several elements which were only present in small amounts, such as nickel and antimony in NBS No. 52 and 63, were not detected in the present analyses because of the proximity of intense X-ray lines from other nearby elements. However, the intent of these studies was to demonstrate the potential of a new method for quantitative elemental analysis which is simple, fairly rapid, and which simultaneously determines all elements over a wide range with comparable sensitivity. It should be evident that extensive improvements could be made by adopting the well known techniques used in conventional X-ray analysis. These may include use of filters, more refined sample preparation techniques, and corrections for matrix effects. In the present work, the electron beam currents used were typically under 100 nA, and the detectors subtended solid angles of the order of  $10^{-3}$ . Since accelerators can easily deliver a thousand times more current, it should be possible to make use of higher resolution



crystal spectrometers to improve the signal to noise ratio without incurring any loss of overall efficiency. Thus, one might anticipate for the future a many-fold increase in the sensitivity of elemental analysis by high energy electron impact ionization.

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