

Dr. J. Conway

IR 64-53
FOR REFERENCE

NOT TO BE TAKEN FROM THIS ROOM

CAT. NO. 4 L.M.CO.

CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

CANMET LIBRARY
555 BOOTH ST
OTTAWA ONT. CANADA
K1A 0G1

IR 64-53

MINES BRANCH INVESTIGATION REPORT ~~IR 64-53~~

APPLICATION OF COMPUTING METHODS TO X-RAY FLUORESCENCE ANALYSIS 5. LEAD ALLOYS

by

MRS. D. J. REED & K. S. MILLIKEN

MINERAL SCIENCES DIVISION

128

COPY NO. 1

This document was produced
by scanning the original publication.
Ce document est le produit d'une
numérisation par balayage
de la publication originale.

JUNE 3, 1964

R/082

Mines Branch Investigation Report IR 64-53

APPLICATION OF COMPUTING METHODS TO X-RAY
FLUORESCENCE ANALYSIS 5. LEAD ALLOYS

by

Mrs. D.J. Reed* and K.S. Milliken**

INTRODUCTION

Previous reports in this series have discussed application of this formula for inter-element enhancement and absorption corrections to stainless steels (2), ores (3) and high temperature alloys (4). The formula has been modified by the addition of a factor for sample size (5) and an exponent for concentration bias (2).

Lead alloys were chosen to test the formula further because Pb, by providing a heavier matrix than any previously used, would markedly increase absorption effects. In addition, the other components, Sn and Sb, could be used to determine if the formula compensated for interfering radiation from adjacent elements.

If P_{nm} and I_{nm} are the percentage and X-ray intensity respectively of the n^{th} element in the m^{th} sample of a group of alloys, the Lucas-Tooth and Price equation (1) for a particular element in an alloy may be written

$$P_{nm} = a_n + I_{nm} (K_{no} + \sum_x K_{nx} I_{xm})$$

The a and K 's are constants derived empirically from X-ray analysis of standard alloys whose range of composition must include that of the unknown.

* Senior Scientific Officer, Analytical Chemistry Subdivision, Mineral Sciences Division and ** Senior Scientific Officer, Metal Physics Section, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

CHOICE OF CRYSTAL

The original claim for the formula did not extend beyond correction of enhancement and absorption. In previous work, when elements adjacent in the periodic table were present (2,4), a quartz crystal was used to separate their characteristic radiation as effectively as possible.

The intensity of radiation reflected from a quartz crystal is much less than that of the same radiation reflected from LiF. For Sb K radiation the ratio was 1:5 as Figure 1 shows. With such reduction in intensity, inter-element effects are less pronounced when quartz is used. LiF reflects a greater proportion of X-radiation than other crystals in common use and hence any modification is more readily observed. This property was a factor in the decision to use LiF to analyse lead alloys.

LiF has disadvantages when used for adjacent elements with $Z > 42$, as illustrated in Figure 1 which compares partial scans of a lead alloy using LiF and quartz. Although quartz does not fully separate the characteristic radiation of Sn and Sb, with LiF, Sn is visible only as a slight inflection on the side of the Sb peaks. Compensation for overlapping peaks in this latter instance would be a major test of the extended use of the formula. This was the prime reason for using LiF as the analysing crystal for these alloys.

STANDARDS AND COUNTING CONDITIONS

Because three elements were to be determined, five samples were necessary to establish the inter-element coefficients. From the small number of spectrographic standards available five were chosen to give as wide a range of Sn and Sb as possible. These were in the form of thick discs of uneven surface in which the identifying numbers were deeply imprinted. Their composition is given in Table 1. A sixth sample, G, was included provisionally. This sample was of adequate area and was composed of two thin strips; it was added to provide a sample beyond the minimum $n + 2$ and to check the effect of physical differences.

Counts were taken on Sn and Sb K_{α} peaks and PbL_{α} and $L_{\beta 1+2}$. The principal L_{β} peaks of Pb occur together making the combined peak the most sensitive for the element. There is a significant difference in energy between PbL_{α} and PbL_{β} radiation. For the little additional counting time required, it was decided to use both to determine whether their contribution or response differed.

The response of the counting equipment is not linear above 80,000 cps so it was necessary to keep Pb counts below this level. At the same time a potential greater than 30.4 kV had to be used. This is the critical potential for Sb K radiation. At 36 kV $PbL_{\beta 1+2}$ for sample G gave 73,000 cps. This potential was used initially although it provided little sensitivity for Sb and Sn.

The counts were repeated using potentials approximately twice the critical potentials in question: 60 kV for Sn and Sb K and 30 kV for PbL radiation. It was assumed that the formula would compensate for intensity variation due to kV because it had done so for intensity differences from two crystals in the case of high temperature alloys, where LiF had been used to count Ti and quartz for all other elements (4).

The higher potential greatly increased Sn and Sb counts, though not by any simple ratio. As Figure 2 demonstrates, the ratio of counts at 60 kV to those at 36 kV was found to vary with the amount of the elements present resulting in a curve that became asymptotic at 6%. The circled Sb value in the figure is for sample G.

Counts were made with the three potentials using 20 ma, an amplifier gain of 10, a baseline of 6V and a scintillation counter tension of 1050V. At 36 kV background counts were taken for Sn and Sb in an attempt to increase the sensitivity of their response. At 60 kV, when Sb and Sn response was enhanced by increased potential, backgrounds were not counted.

PROGRAMS SUBMITTED TO COMPUTER AND RESULTS

Three groups of results were submitted to the computer for analysis by the Lucas-Tooth and Price formula:

Program A:

Net counts on all samples at 36 kV with counts for both Pb peaks comprised the first group. A value of 0.5 was used for the exponent E.

The results are shown in Table 2. The effect of physical condition is immediately apparent in sample G results. The difference in this sample could be responsible for discrepancies in the other results. There is no comprehensive significant difference due to the different Pb radiations.

Program B:

The second results computed were produced from the first five samples only and are the total counts using different kV's. PbL_{β} radiation was used and an E of 1 to favour low concentrations.

Program C:

The counts of Program A were resubmitted minus sample G using PbL_{β} radiation and an exponent of 1. These results were necessary for the proper evaluation of Program B.

Results from Programs B and C are shown in Table 3. Both give excellent agreement with the certified analysis.

EVALUATION OF FORMULA

To evaluate properly what was accomplished by the use of the formula regression lines for Sn and Sb were calculated from the counts of Program B and results were determined using these equations. They are compared with Program B results in Table 4. The improvement in Sb analysis resulting from the use of the formula is marked in three cases. Sn results all improved when the formula was used, but not all differences are significant.

The total counts for Pb showed such a wide scatter that regression was meaningless - Figure 3 (a). The vast improvement with the formula is evident in Figure 3 (b).

For interest, the coefficients determined by the formula and used in determining the results are listed in Table 5 for Programs B and C. As would be expected, there is a significant difference in all Sb and Sn coefficients when the background is not determined. From the values of 'a' for Pb it is obvious that extrapolation to lower Pb concentrations is not possible. The prohibition of the upward extension of Sn and Sb concentrations is not readily apparent, but may be inferred by reflection of the Pb error in them. Remarks by Ezekiel (6) regarding the extrapolation of simple regression may be applied here.

CONCLUSIONS

Lead alloys have been successfully analysed for three components using the Lucas-Tooth and Price formula.

The formula was successful in compensating for interfering radiation in this case as well as for general absorption and enhancement effects.

Samples must be of the same physical nature.

Counts need not be corrected for background.

The use of different potentials for different elements is possible as long as the kV is consistent for each peak.

The final equations should not be extrapolated to concentrations beyond those used to establish their coefficients.

ACKNOWLEDGEMENT

Counts for Program A were made by Mrs. M.K. Allan.

REFERENCES

1. Lucas-Tooth, H.J., and Price, B.J., "A Mathematical Method for the Investigation of Inter-element Effects in X-ray Fluorescent Analysis", Metallurgia 64, 149, 1961.
2. Gillieson, A.H., Milliken, K.S. and Young, M.J., "The Application of Computing Methods to X-ray Fluorescence Analysis. 1. Stainless Steel", Mines Branch Investigation Report IR 62-25, December, 1962.
3. Gillieson, A.H., and Young, M.J., "The Application of Computing Methods to X-ray Fluorescence Analysis. 2. Copper in Ores", Mines Branch Investigation Report IR 62-26, May, 1962.
4. Gillieson, A.H., Milliken, K.S. and Young, M.J., "The Application of Computing Methods to X-ray Fluorescence Analysis. 4. High Temperature Alloys", Mines Branch Investigation Report IR 63-52 (in draft).
5. Gillieson, A.H., Milliken, K.S. and Young, M.J., "The Application of Computing Methods to X-ray Fluorescence Analysis. 3. Mathematical Derivation of a Correction Factor to Compensate for Variations in Surface Finish and Size of Samples", Mines Branch Investigation Report IR 63-51, February, 1963.
6. Ezekiel, M., "Methods of Correlation Analysis". John Wiley and Sons, 1953, p. 126.

DJR:CL:ST

TABLE 1

Composition of Samples

| | % Pb | % Sb | % Sn |
|------|-------|-------|------|
| 502 | 88.55 | 11.02 | 0.10 |
| 506 | 79.91 | 17.94 | 1.52 |
| 512 | 97.30 | 2.06 | 0.48 |
| 516 | 93.00 | 6.13 | 0.53 |
| 1010 | 99.94 | 0.00 | 0.00 |
| G | 98.70 | 1.06 | 0.04 |

TABLE 2

Results Using Different Lead Peaks

| | % Pb | | % Sb | | % Sn | |
|------|----------------|----------------|----------------|----------------|----------------|----------------|
| | L _a | L _B | L _a | L _B | L _a | L _B |
| 502 | 88.64 | 88.49 | 10.73 | 10.81 | 0.08 | 0.09 |
| 506 | 79.89 | 79.91 | 18.17 | 18.20 | 1.53 | 1.53 |
| 512 | 97.40 | 97.16 | 1.58 | 1.79 | 0.44 | 0.47 |
| 516 | 93.25 | 93.15 | 5.57 | 5.28 | 0.53 | 0.48 |
| 1010 | 100.52 | 100.04 | - 0.01 | - 0.01 | -0.01 | -0.01 |
| G | 97.67 | 98.61 | 2.15 | 2.12 | 0.13 | 0.12 |

TABLE 3

Results by Programs B and C

| | % Pb | | % Sb | | % Sn | |
|------|-------|-------|-------|-------|------|------|
| | B | C | B | C | B | C |
| 502 | 88.55 | 88.53 | 11.01 | 11.02 | 0.10 | 0.09 |
| 506 | 79.90 | 79.91 | 17.93 | 17.94 | 1.52 | 1.51 |
| 512 | 97.30 | 97.26 | 2.05 | 2.06 | 0.48 | 0.47 |
| 516 | 92.99 | 93.02 | 6.13 | 6.12 | 0.52 | 0.53 |
| 1010 | 99.93 | 99.96 | 0.00 | 0.00 | 0.00 | 0.00 |

TABLE 4

Results by Program B and Linear Regression

| | % Sb | | % Sn | |
|------|-------|-------|------|------|
| | B | Reg. | B | Reg. |
| 502 | 11.01 | 9.91 | 0.10 | 0.20 |
| 506 | 17.93 | 18.50 | 1.52 | 1.54 |
| 512 | 2.05 | 2.11 | 0.48 | 0.41 |
| 516 | 6.13 | 6.11 | 0.52 | 0.48 |
| 1010 | 0.00 | 0.51 | 0.00 | 0.00 |

TABLE 5

Coefficients for Programs B and C

| Element | $\frac{a}{\cdot X10^{-1}}$ | $\frac{K_o}{X10^{-3}}$ | $\frac{K_{Sb}}{X10^{-6}}$ | $\frac{K_{Sn}}{X10^{-6}}$ | $\frac{K_{Pb}}{X10^{-6}}$ |
|---------|----------------------------|------------------------|---------------------------|---------------------------|---------------------------|
| | | <u>Program B</u> | | | |
| Sb | -3.881107 | 2.167096 | -0.004286 | -0.041195 | -0.031015 |
| Sn | -1.595705 | -0.499184 | -0.003626 | 0.052390 | 0.014011 |
| Pb | 1548.1554 | -2.655320 | -0.009606 | -0.002696 | 0.031268 |
| | | <u>Program C</u> | | | |
| Sb | -1.642913 | 13.431742 | -0.131644 | -2.003996 | -0.129985 |
| Sn | -0.631690 | -4.459392 | -0.220903 | 2.787236 | 0.079235 |
| Pb | 1561.9715 | -1.849066 | -0.048640 | -0.020751 | 0.014933 |

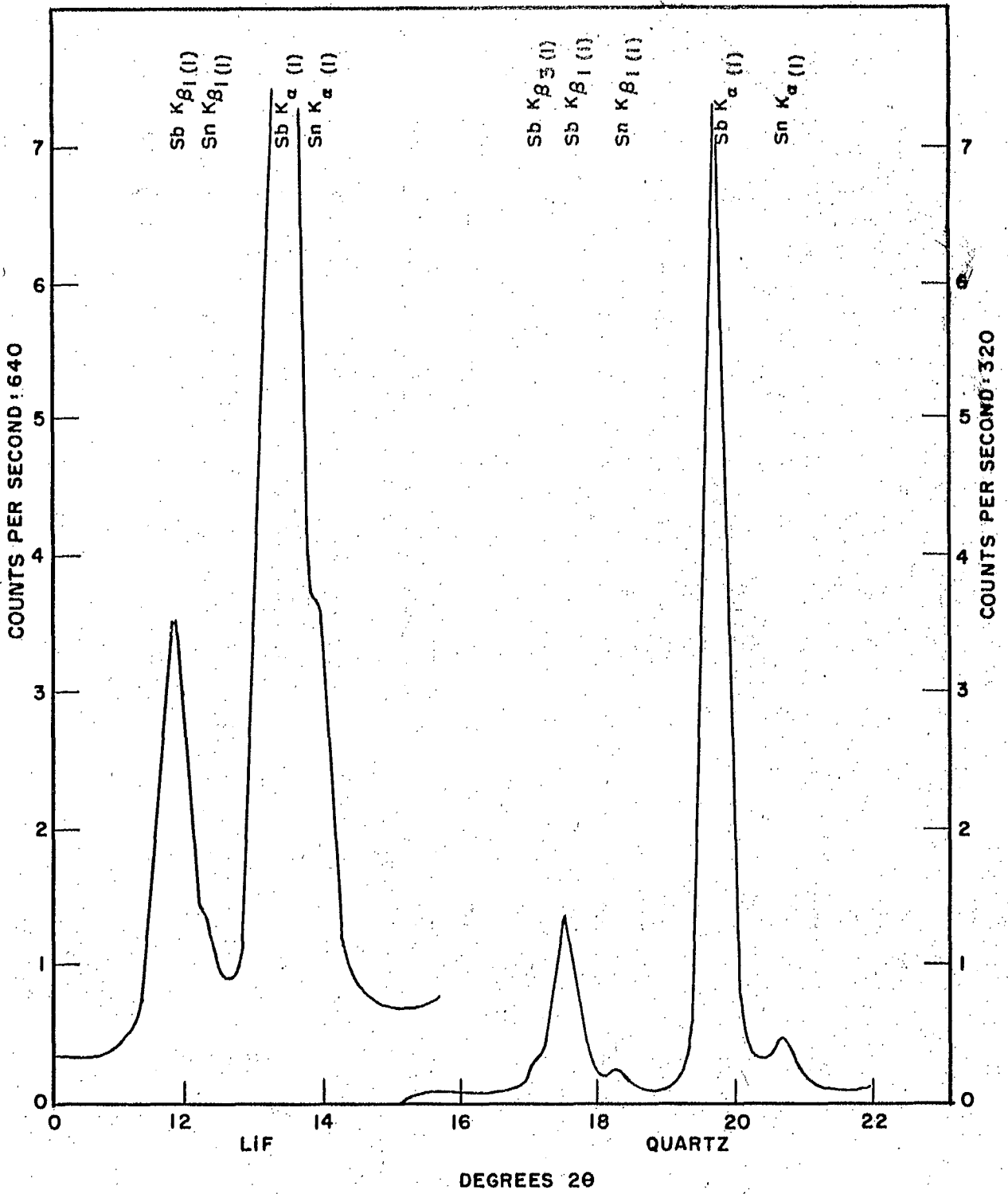


FIGURE 1: SCANS OF SAMPLE 506 WITH DIFFERENT ANALYSING CRYSTALS.

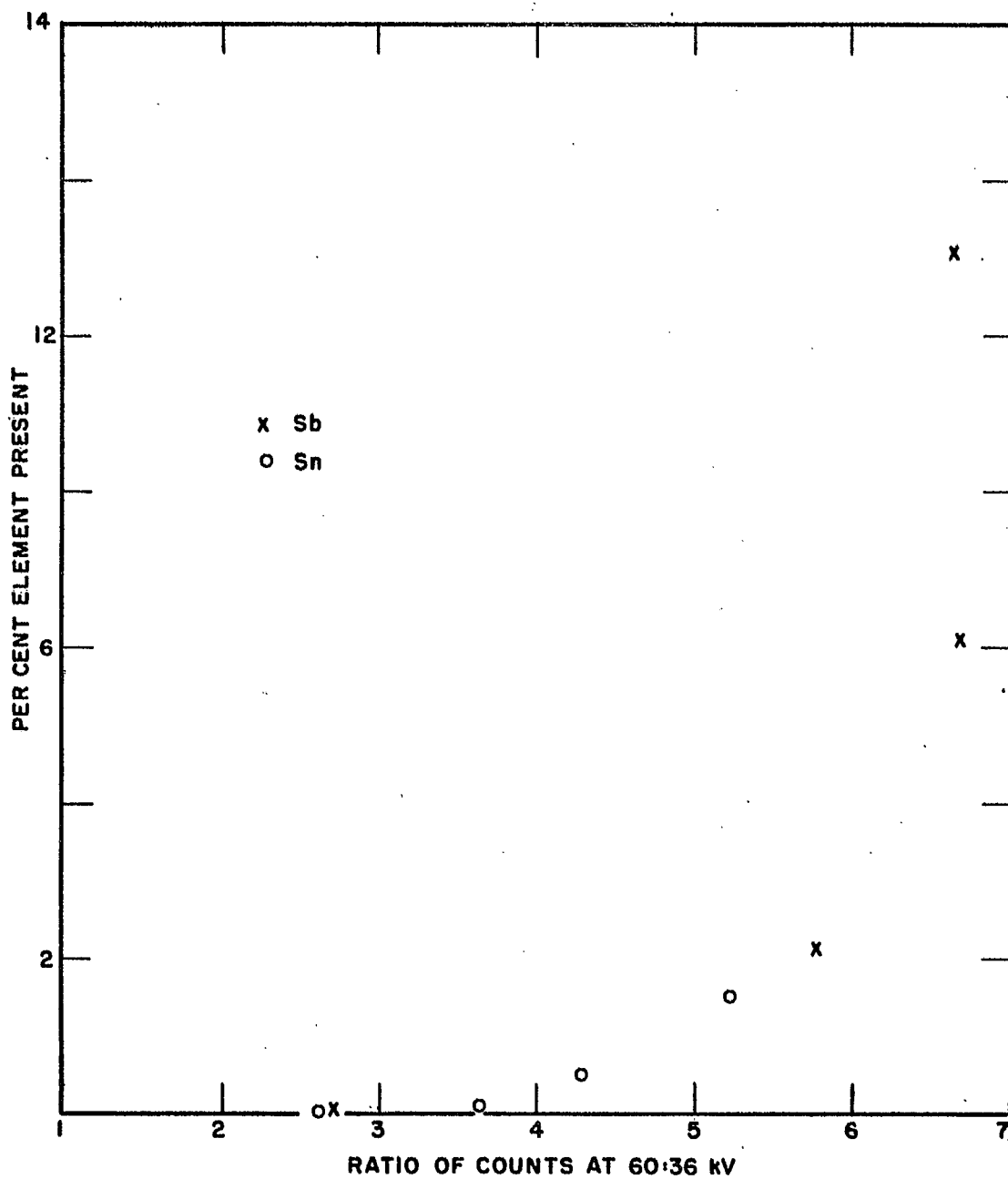


FIGURE 2: VARIATION IN COUNT RATIO WITH CONCENTRATION

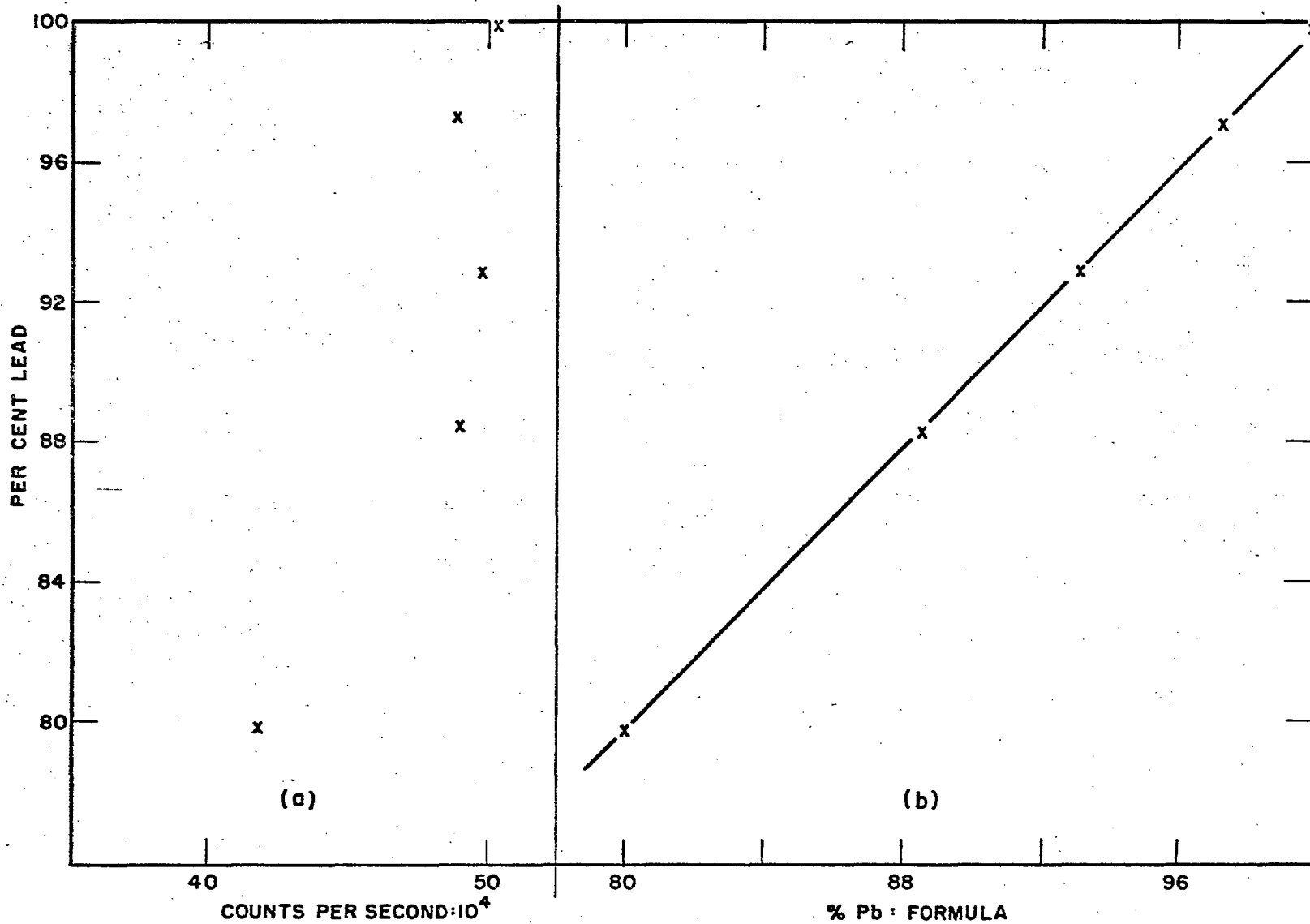


FIGURE 3: % LEAD AND X-RAY RESULTS, PROGRAM: a-TOTAL COUNTS, b-FORMULA RESULTS.