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Determination of Ion Intensities from Spark Source Mass Spectrometry Photoplates

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A method is described which allows quantitative lines of a spark source mass spectrum on a photographic plate to be represented by three parameters only. These three parameters are the maximum absorption of the line, background, and the area produced by an integrator when the line is scanned on a microdensitometer. From these three data, plus the measured response characteristics of the photographic plate, a mathematical technique is described which yields the total number of ions which produced the line. A digital computer program is used in carrying out the mathematical method. The only assumption made is that the intensity of the beam which produced the line followed a normal (Gaussian) distribution about the point of maximum darkening.

INDEX HEADINGS: Mass spectroscopy, spark source; Densitometry; Computer, applications.

INTRODUCTION

Elemental sensitivities for the spark source mass spectrometer are relatively equal as compared to other methods for trace analysis. There are many parameters, however, that can affect the data to varying degrees.

It has been recognized that peak width variations due to source parameters, focusing conditions, isotopic mass, and space charge effects[1-3] can cause gross differences in elemental sensitivity. These effects can be reduced by carefully controlled experimental conditions,[3] but in actual practice, where widely varying electrode shapes and materials are encountered, close control of source parameters is difficult or impossible.

Focusing variations have been successfully corrected by manually measuring the peak width after conversion to intensity.[2] Peak area integration is also used to accomplish this purpose. Integration may be performed by analog computer after linearization of the signal from the densitometer.

If, however, one wishes to take advantage of the accuracy, convenience, speed, and storage capacity of a digital computer, either the errors intrinsic in using absorption maxima must be accepted or a means must be found to correct digitally for variations in peak width.

Woolston and Botnick[4] were among the first to use the digital computer for photoplate data reduction. They transferred about 100 blackening data points equally spaced across a spectral line to punched tape. These data, after transfer to a computer, were converted point by point to intensity via the Hull equation.[5] Area under the intensity peak could then be computed, giving an accurate representation of relative ion beam intensity. This technique generally requires the collection of massive quantities of data from the photoplate.[6]

A method is described in this paper in which the computer simulates an intensity peak from three data parameters: (1) area under the densitometer tracing of a line on the photoplate; (2) the maximum percent absorption of that line; and (3) the average plate blackening or background in the vicinity of the line.

These data can be collected with a microdensitometer and a simple electronic integrator.

I. INSTRUMENTATION

A C.E.C. 21–110 spark source mass spectrometer was used at 25 kV accelerating potential. The instrument was modified so that very fine screens (500 mesh, custom made by Buckbee Mears Corp., St. Paul, Minn.) of known open area could be manipulated into position, via a bellows seal, to intercept portions of the ion beam in the flight tube and thus reduce the ion current without alteration of source parameters. This apparatus is described in another publication.[7] Ion beam attenuations up to 100:1 could be effected in this manner.

A Jarrell Ash recording mirodensitometer was used to scan the isotopic lines, and a Heath Universal Digital Instrument integrated the lines as they were scanned on the densitometer. An offset voltage equal to the average background signal adjacent to the peaks was applied to the integrator so that background was continuously subtracted from the peaks during this integration.

The data were typed into punched cards and processed by a Control Data 6000 series computer under remote batch entry.

II. PROCEDURE

Tin was selected for data collection because of the large number of isotopes with wide variations of concentration. Source parameters were adjusted to obtain a high intensity ion beam. If the beam attenuator described above is not used, severe broadening of the lines occurs. Under the same conditions, use of the attenuator produced sharply focused lines.

III. MATHEMATICAL MODEL

Assuming that the ions of a given spectral line in a mass spectrometer hit the photographic plate over a certain interval in the beam deflection direction, and that the intensity of the impacting ions obeys a Gaussian distribution, the following equation can be written:

$$I(x) = I_{\max} e^{-x^2/2\sigma^2} \tag{1}$$

where $I(x)$ = beam intensity at location x along the beam deflection direction; $I_{\max}$ = intensity at point of maximum blackening. The origin is chosen so that at this point $x = 0$. σ = dispersion of the Gaussian curve about its mean at $x = 0$.

If the number of impinging ions in the entire spectral line under consideration is represented by Z, one can write:

$$Z = \int_{-\infty}^{\infty} I(x)\, dx = I_{\max} \int_{-\infty}^{\infty} e^{-x^2/2\sigma^2}\, dx \tag{2}$$

The definite integral of the Gaussian function yields

$$Z = I_{\max}\sigma\sqrt{2\pi} \tag{3}$$

A technique for finding σ in the above equation follows.

When the photographic plate has been calibrated, the beam intensity can be related to the absorption, A, of a light beam passing through the darkened area:

$$I = P(A) \tag{4}$$

where P may represent the Hull equation,[5] or a polynomial approximation to the response curve, or any other function which yields intensity from absorption. The parameters of P have to be evaluated experimentally. It is assumed that its inverse function, P^*, is also known, so that given any intensity, I, we may write:

$$A = P^*(I) \tag{5}$$

The experimentalist may measure, without undue difficulty, two parameters describing each spectral line. These are the maximum absorption, $A_{\max}$, and the area under the absorption curve, R.

If it is assumed that the incident beam which produced the line obeyed Eq. (1), then,

$$R = \int_{-\infty}^{\infty} A(x)\, dx = \int_{-\infty}^{\infty} P^*\{I(x)\}\, dx = 2\int_{0}^{\infty} P^*\{I_{\max} e^{-x^2/2\sigma^2}\}\, dx \tag{6}$$

in which $I_{\max}$ can be obtained by substituting $A_{\max}$ for A in Eq. (4).

The integral in Eq. (6) may be approximated by a finite sum of slices of width Δx and may thus be evaluated by a digital computer. For all practical purposes, the sum of the area of these slices will approximate the value of the integral with sufficient accuracy if (1)

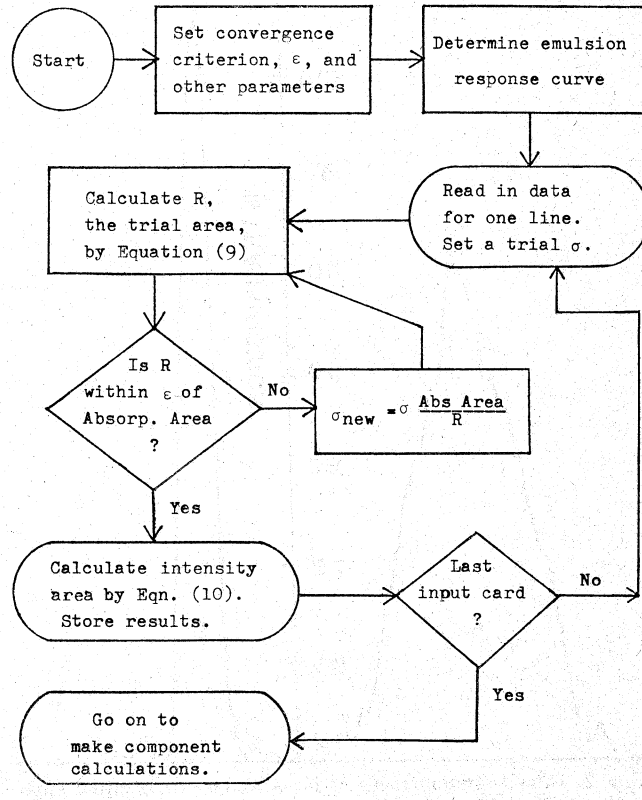

FIG. 1. Flow chart for determination of intensity area.

the step-size Δx is chosen to be 0.05σ, and (2) the summation is extended out to 5σ from the origin. Therefore, a Fortran program was written to evaluate the following expression:

$$R_{\text{trial}} = 2\sum_{x=0}^{5\sigma} P^*\{I_{\max} e^{-x^2/2\sigma^2}\}\Delta x \qquad (7)$$

The computer program searches for a σ which will make the sum in Eq. (7) sufficiently close to the experimentally measured absorption area. To this end, a trial value, σ_{trial}, is chosen and used in evaluating the right-hand side of Eq. (7). If the resulting R_{trial} is smaller than R, then a larger σ is chosen and the summation is done again. This trial-and-error technique is continued until a σ is found which yields an area suitably close to that which was measured experimentally. A simplified flow chart of this computer program is shown in Fig. 1.

Of course, it is not necessary to carry out the summation to the full $\pm 5\sigma$ width. The program does not evaluate to beyond the point where the absorption falls to the lowest point measured on the emulsion response curve. This avoids errors due to extrapolation outside the proper range. Also, the search for σ can be shortened considerably when the second σ_{trial} is chosen as (R/R_{trial}) times the first σ.

The final σ is then a measure of the dispersion of the incident beam which yields the experimentally observed area under the absorpton curve. The "intensity area," which is a measure of the number of ions which produced the spectral line, is found by substituting this value of σ into Eq. (3). The units in which the answer is expressed will depend on experimental conditions and the characteristics of the instruments used, and they should be adjusted to the proper units by comparison with a line or series produced by a known concentration and known exposure.

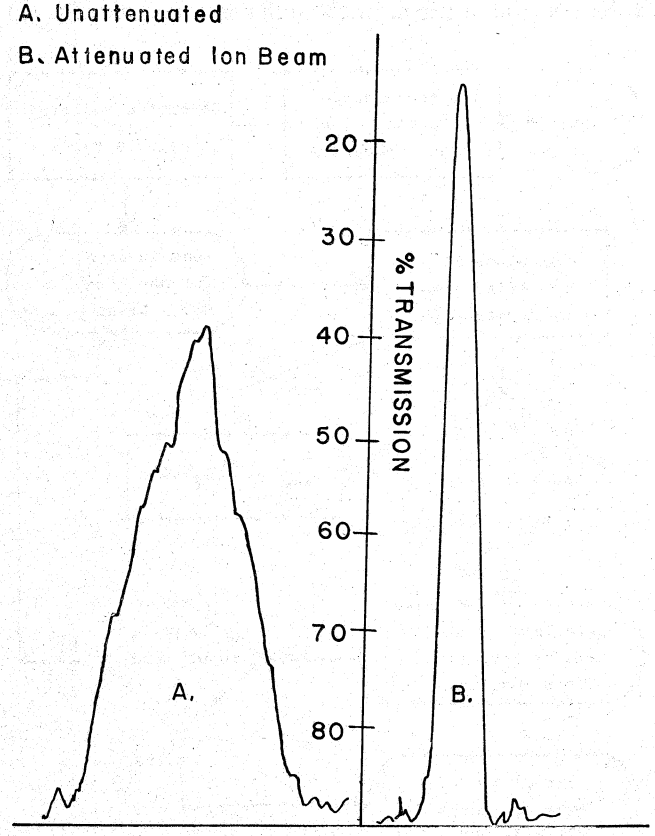

FIG. 2. Densitometer traces of lines representing equal exposures of $^{118}Sn^+$ (5×10^{-12} C).

IV. CORRECTION FOR BACKGROUND

A blackening of the emulsion surrounding the lines is usually experienced during the exposure, so that Eq. (1) should be modified to:

$$I(x) = I_{\text{bkg}} + (I_{\max} - I_{\text{bkg}})e^{-x^2/2\sigma^2} \qquad (8)$$

where I_{bkg} = ion intensity which would produce the equivalent local background; $I_{\max}$ = maximum intensity of the spectral line, including effect due to local background.

Some disagreement exists between authors about the methods of background correction. Kennicott treats this subject on page 182 of a yet unpublished book.[8] The assumption will be made that plate blackening due to secondary ions follows the same emulsion response characteristics as for the primary ion beam and that the peak blackening and background are additive.[2, 9] Representing background absorption by B, the area measured is therefore:

$$\begin{aligned} R &= \int_{-\infty}^{\infty} [A(x) - B]\,dx \\ &= \int_{-\infty}^{\infty} [P^*\{I_{\text{bkg}} + (I_{\max} - I_{\text{bkg}})e^{-x^2/2\sigma^2}\} - B]\,dx \qquad (9) \\ &\approx 2\sum_{x=0}^{5\sigma} [P^*\{I_{\text{bkg}} + (I_{\max} - I_{\text{bkg}})e^{-x^2/2\sigma^2}\} - B]\Delta x \end{aligned}$$

When a proper σ is found to satisfy Eq. (9), it can be substituted into the following equation to yield a measure of the total number of ions:

$$Z = (I_{\max} - I_{\text{bkg}})\sigma\sqrt{2\pi} \qquad (10)$$

Eq. (9) and (10) are the more general forms of Eq. (7) and (3), respectively.

V. RESULTS AND CONCLUSIONS

Three exposures of tin were made. Two of the exposures were identical at 5×10^{-12} C with the exception that a 1% open area screen was used in one case. Fig. 2 shows a comparison of the $^{118}Sn^+$ lines from the two equal exposures, recorded by the densitometer at the same rate of scan. As can be seen, the unattenuated peak is approximately three times as broad as the peak on the right, and its maximum blackening is less. The computer program, however, correctly calculated that both peaks represent an equal number of ions arriving at the photoplate.

Fig. 3 is a computer-generated plot, drawn on a CalComp plotter, of log intensity vs log (exposure $\times$ isotopic abundance) for the three exposures. All isotopes of tin are represented. On this plot, relative ion abundances were calculated by the peak height method.

Valid data points should fall on a straight line of slope 45°. Note that poorly focused lines (from the unattenuated exposure) give data points which fall below the well focused lines. Furthermore, the slope of the two lines is about 0.85, rather than 1.0. This is explained by two factors. (1) The peaks of lower abundance isotopes generally had smaller values for sigma than did peaks of more abundant isotopes, which was apparently due to space charge effects. The greater dispersion of the more abundant isotopes would tend to reduce values at the upper end of the line. (2) For this experiment, plate response characteristics were not taken from the same photoplate as the one used in the determination of isotopic intensities of tin; consequently, differences in sensitivity factor between the two plates could influence the slope of the line.

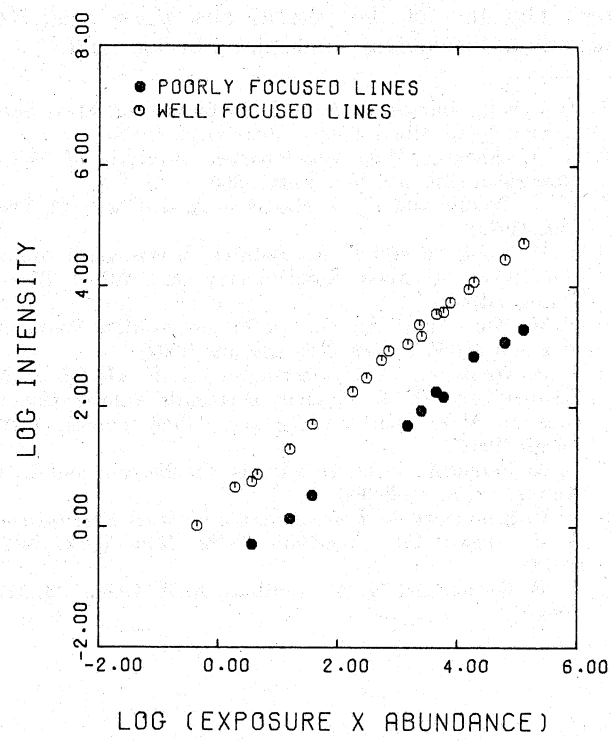

FIG. 3. Theoretical intensity vs measured response of isotopes of tin. No area correction applied.

Fig. 4 is a similar plot from the same data after the mathematical area correction has been applied. As can be seen, all the corrected data give points that fall on the same straight line, within experimental error. The slope is now much closer to 1.0, reflecting the improvement in results when the area correction technique is used.

To demonstrate that the slight variation of the slope from 1.0 was due to the aforementioned difference in sensitivity of the emulsion response plate, another exposure was analyzed using an emulsion response curve which more accurately described the plate characteristics. This experiment is represented by Fig. 5. Points at each end of the graph should be excluded in such an estimation of slope. The three points of lowest intensity approach the noise level of the plate, whereas the two highest points are near plate saturation. When these five points were eliminated from consideration, a statistical analysis showed that the slope of the least

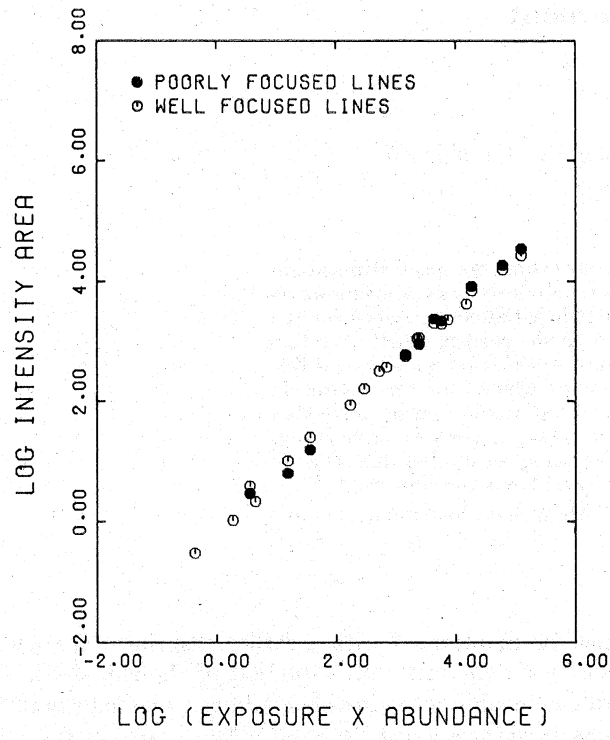

FIG. 4. Theoretical intensity vs measured response of isotopes of tin. Area correction applied. Emulsion response in Figs. 3 and 4 was derived from another plate with the same lot number.

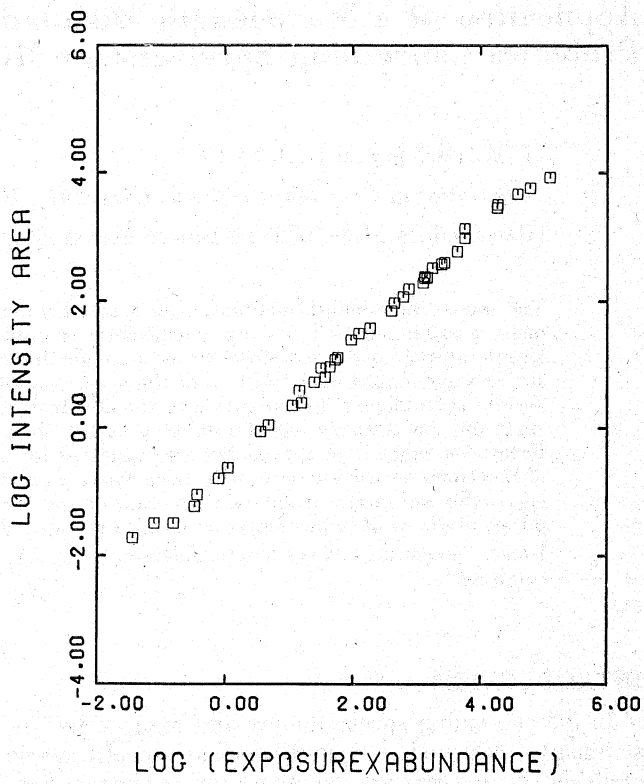

FIG. 5. Theoretical intensity vs measured response of isotopes of tin. Area correction applied. Emulsion response curve was determined directly for this plate.

squares line of Fig. 5 is 0.997, which is less than one-third standard deviation away from the theoretical ideal of 1.000.

The data range in Figs. 3 and 4 covers from 9 to 82% absorption, whereas in Fig. 5 the range is from 8 to 97%.

The basic assumption of this technique is that the ion beam obeys a Gaussian distribution about the point of maximum blackening. In our instrument, the lighter elements often produce asymmetrical spectral lines, which indicates that, for these elements, a Gaussian distribution is not strictly followed. However, a plot similar to Fig. 5 with 24 markedly asymmetrical silicon peaks gave a slope of 0.98 ± 0.06 at the 95% confidence level. Asymmetrical peaks of light elements have been corrected by this technique and compared with the responses of symmetrical peaks from heavier elements. This brought the response of the lighter elements into line with the response of the heavier elements, when corrected for mass differences.[7]

VI. SUMMARY

The mathematical method described, which might be called the "sigma-correction" technique, successfully corrects for line width variations under extreme circumstances. The several physical causes of these variations need not be considered, as long as their net effect is to produce a Gaussian diffusion of the incident beam. With this assumption, the experimentalist needs only three bits of information relative to each line: The area of the percent absorption peak, the maximum blackening, and plate background.

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Application of a Wave-length Modulation Device to Problems Concerning Spectrometer Misalignment

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The use of wave-length modulation as a tool for minimizing spectrometer spectral misalignment is examined. A vibrating quartz plate is employed to repetitively scan a small wave-length interval at the exit slit of a spectrometer. Increased latitude is thereby provided for any slit or wave-length misalignment of the spectrometer, as long as the correct signal detection system is employed. Investigation of the effects of wave-length modulation on a typical line spectrum has revealed signal averaging as the optimum detection system for this approach. From this, additional approaches are suggested for manual and automatic routine correction of spectrometer wave-length drift using existing optical systems. Also, a new technique is suggested for automatic feedback correction of the spectrometer using an on-line digital computer. Methods of implementation of all these procedures are considered and discussed.

INDEX HEADINGS: Wave-length modulation spectroscopy; Alignment correction; On-line computer.

INTRODUCTION

In direct reading spectrometers and many other instruments designed for multielement spectrometric analysis, it is necessary to maintain accurate alignment throughout the optical system. In particular, the location and positioning of exit slits or slit arrays must be maintained within rather exacting tolerances, usually on the order of a fraction of the slit width, in order to enable reproducible readings to be maintained. Such tolerances must be observed not only in the initial alignment but also in the long term stability of the entire system. Thermal fluctuations, changes in