A PROCEDURE FOR
SPECTROGRAPHIC ANALYSIS
OF PLANT ASH

by

ARTHUR RICHARD TYNES

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APPROVED:

Redacted for privacy

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Professor of Physics

In Charge of Major

Redacted for privacy

_____

Head of Department of Physics

Redacted for privacy

_____

Chairman of School Graduate Committee

Redacted for privacy

_____

Dean of Graduate School

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Typed by Mary Kittams Tynes

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INTRODUCTION

It is intended that this paper will have a two-fold purpose: first, to furnish a procedure for quantitative spectrographic analysis of a number of chemical elements in plant ash samples; and second, to permit one to make a rapid qualitative evaluation of additional elements. The qualitative evaluations might then serve as a guide for further chemical analyses.

The procedure outlined below may seem somewhat unorthodox and, therefore, a word of explanation is in order. The objective is to develop a procedure for quantitative analysis and at the same time develop it in such a manner that it may easily be extended to include a much larger number of elements. In this connection the elements have been divided into three groups according to their volatilities. This division necessitates three arcings for each sample - one for each group of elements. Because of the very high volatility rates of Zn and Cd, it has been found necessary to use a different type of electrode for these two elements. The last two less volatile groups of elements require the same type of electrode and, in fact, the same electrode is arced twice in identically the same manner. The procedure for arcing

is described in a later section. The first column in
Fig. 1 below shows the elements for which a procedure has
already been developed, whereas the second column shows
the elements which it is intended the method will eventu-
ally include.

Group	Included	To Be Included
I	Zn, Cd	As, Hg, Rb, Pb, Cs, Bi, In
II	Cu, Mo	Ag, Li, Sb
III	Co, Fe	Ba, Sr, Al, Be

Fig. 1

A fourth group of the very involatile elements, such
as Zr, Nd, Th, Ce, Pt and Ti, might be analyzed by arcing
the electrode used for Group II and Group III for the
third time. This would be only one of many possible pro-
cedures.

All working curves were constructed using the prin-
ciple of internal standards. In this method a constant
amount of the internal standard element is added to all
samples and the ratio of intensity of the analysis line
and the internal standard line is then calculated. A
series of samples of known concentration of trace elements
is then prepared, internal standards added, and arced.
From data of the resulting spectrograms the intensity

ratio is calculated and plotted as the ordinate on log-log coordinate paper and concentration is plotted as the abscissa. The points are then connected by a smooth curve. This curve is called the working curve and all subsequent intensity ratios are referred to this curve in order to determine concentration of the trace elements. The correction of the working curve for effects such as self-absorption and residual impurities is discussed in a later section.

EQUIPMENT

Spectrograph

The spectrograph used for this analysis is a Jarrell-
Ash Company, 480cm, Wadsworth mounting concave grating
spectrograph. This particular type of mounting not only
produces a stigmatic image but a very near linear disper-
sion. Such a linear dispersion makes interpolation
between known lines much simpler and more accurate.

This instrument has a guaranteed resolution of 0.07A
and a linear dispersion of 7A/mm in the first order
spectrum. Thus with this resolution, the identification
of spectrum lines lying very close to interfering lines
is made much easier. With a linear dispersion of 7A/mm,
the spectral range from 2500-3500A will require about six
inches of film. One four-inch by ten-inch photographic
plate will, therefore, serve to photograph the whole of
the spectral range generally used in quantitative work.

Power Source

The excitation unit used is a National Spectrographic
Laboratories "Spec-Power." This unit provides power for a
low voltage direct current arc, an alternating current
arc, and a high frequency spark. The operator may change
the mode of excitation very easily. Incorporated in this
unit is a pre-arc timer and a timer which controls the

exposure by opening and closing a shutter behind the spectrograph slit. Once having properly set these timers, the pre-arcing time and exposure time is controlled automatically for as long a period as desired.

The Physics Department here at Oregon State College has constructed a spark unit for the electrical ignition of the spectrographic arc. With this unit a high-potential, high-frequency voltage of low energy is superimposed upon the direct current supply so that the arc gap is readily bridged. Once bridged, the arc is maintained by the direct current supply. This unit is also used to initiate the A.C. arc.

Microphotometer

For measuring the blackening of the spectral lines a Jarrell-Ash Company Projection Comparator Microphotometer (Catalog No. JA-200) is used. This instrument projects the image of a master spectrogram just adjacent to the spectrogram which is to be measured. In this way positive identification of spectrum lines is assured. In this manner not only quantitative information but qualitative information as well is obtained.

QUALITATIVE EVALUATION OF THE SPECTROGRAMS

The first step in preparing master plates is to locate a large number of Fe lines in the Fe spectrum. This is very easily accomplished with the aid of the very extensive photograph of the Fe spectrum contained in the appendix of Brode (2, pp.447-482). Once having located these Fe lines, the sensitive lines of the various elements are easily identified and labeled with the proper wave-length alongside. The master plate is then placed in position on the microphotometer and its image projected just adjacent to the spectrum to be measured. In this manner the sensitive lines in the unknown spectrum are very easily located and measured.

QUANTITATIVE SPECTROGRAPHIC ANALYSIS

Choice of Photographic Emulsion

Because of the rather large variation in wave-lengths of the spectral lines used in this analysis, an emulsion in which the contrast does not vary with wave-length is desirable. For this reason Kodak Spectrum Analysis No. 2 photographic plates were selected for use. Also, the relatively small grain size of this emulsion makes it more desirable from the reproducibility of measurement of line intensity standpoint.

Development of Photographic Plates

A very favorable ratio of intensity of background to intensity of spectral line is obtained if the plates are developed to a gamma of about 1.1. With the use of the calculating board, it is a very easy job to determine the gamma of each plate from the iron spectrum which is always included. For this reason it is not necessary to control development to such a high degree. It was found that if the plates were developed in Kodak D-19 at 20°C for three minutes that the gamma was usually very close to 1.1. The plates are agitated constantly and rinsed in a 1% glacial acetic acid stop bath for 10 seconds and transferred to the hypo for about 10 minutes. The plates are

then washed in tap water for one hour, rinsed with
distilled water and allowed to dry in the air. Wiping
the plates dry with a clean sponge seems to have an
adverse effect on the surface of the emulsion and should
be avoided.

Preparation of the Plant Ash Samples

In order to avoid loss of the more volatile elements
As, Cd, Hg, and Zn, the ashing of the plant samples is
carried out at a temperature of 450°C. This temperature
is maintained for a period of 36 hours. Since the
resulting ash is not entirely free of unburned carbon,
the samples are very easily ground in an agate mortar to
an impalpable fineness, a necessary condition for this
type of analysis.

Preparation of the Standards

It is a well known fact that the rate of emission of
a spectral line depends very much upon the chemical compo-
sition of the base material. For this reason it is
necessary to obtain a base material whose composition
closely approximates that of the ash to be analyzed. On
the basis of information obtained from Dr. J. R. Haag of
the Agricultural Chemistry Department, the base powder
was mixed as shown on page 9.

$$5 \text{ grams } NaCl$$
$$10 \text{ grams } CaCO_3$$
$$3 \text{ grams } Mg_2SO_4 7H_2O$$
$$3 \text{ grams } KH_2PO_4$$
$$10 \text{ grams } K_2CO_3$$
$$\underline{3 \text{ grams } MgO}$$

Total   34 grams

It must be remembered that this is only an average composition of typical samples.

Because it is desired to detect trace elements in very low concentrations, it is necessary that the chemicals used in preparing the base powder be free of these trace elements. For this purpose Johnson-Matthey chemicals obtainable through Jarrell-Ash Company were found to be satisfactory. A slight correction of the working curves for the residual impurities is necessary, however.

The procedure for mixing the standards was to first make a 1% mixture of trace elements in the base powder and to use this to make successive lower concentration standards. No weighing of less than 5mg was made throughout the project. All chemicals were dried in a drying oven before weighing. The drying temperatures are set forth on the following page.

Drying Temperature	Duration	Chemical
300°C	3 hours	NaCl, Tl_2SO_4, GeO_2, Ga_2O_3, PdO, Fe_2O_3, Cr_2O_3, NiO
400°C	4 hours	MoO_3, CuO, $CoCO_3$, ZnO, MnO_2

Standards were mixed for concentrations of 0.86%, 0.40%, 0.185%, 0.086%, etc. down to 0.000086%.

The Internal Standards

The choice of internal standards and the amounts to be used follow closely the recommendations of Vanselow and Liebig (6, p.35). Because of the small amounts of internal standards needed (about 0.005mg per sample), they were mixed with the pure base powder and this mixture then was added as the internal standard. The composition of this mixture is

> 3.0 grams of base powder
> 5.0 mg GeO_2
> 5.0 mg PdO
> 5.0 mg Tl_2SO_4
> 5.0 mg Ga_2O_3

Ga_2O_3 was added as an internal standard for Cu and Mo after it was discovered from a time study that Ga constitutes a better internal standard for these elements than Ge. Fig. 2 illustrates data obtained from such a

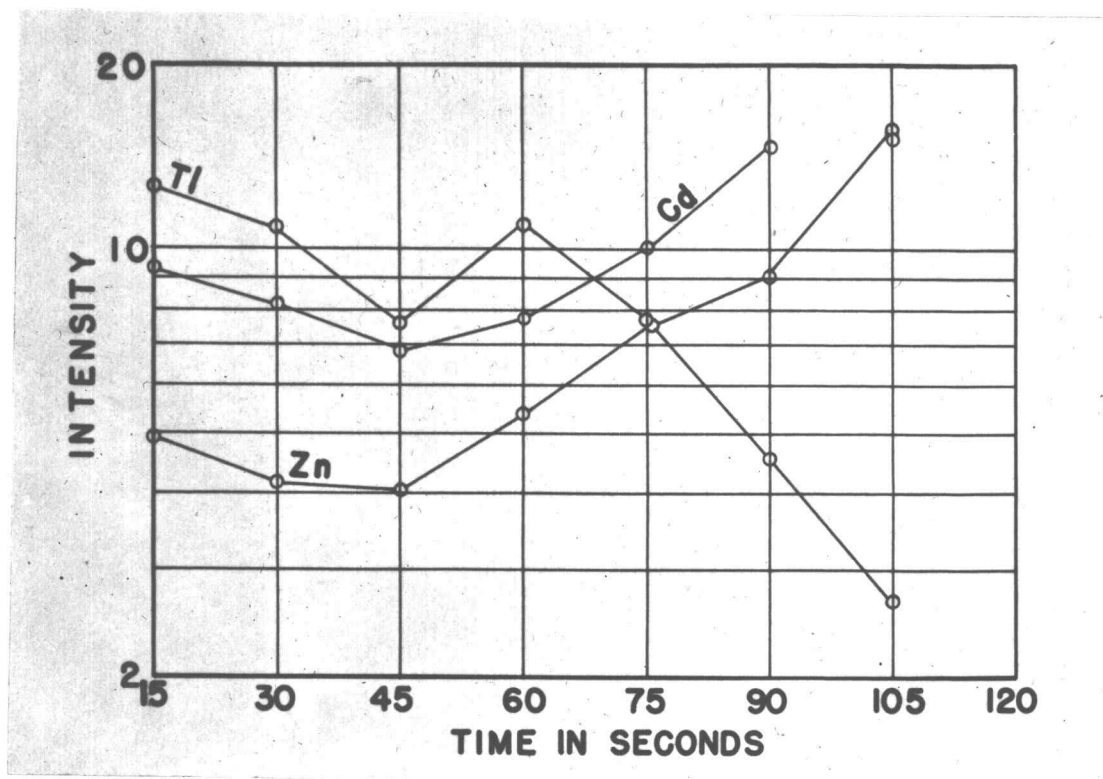time study of the burning of Cd and Zn with Tl as the
internal standard.

Fig. 2

The data represented in Fig. 2 were obtained in the
following manner. A single electrode was filled with a
standard sample containing 1000 parts per million of Cd
and Zn and the proper amount of the internal standard
mixture. The electrode was then placed in the electrode
holder and the arcing cycle was started. The sample was
burned continuously for two minutes. Time intervals of
15 seconds duration were counted, the first interval
ending 15 seconds after the arc was initiated. At the
end of each time interval, the photographic plate was

racked to a new position. In this manner a series of
spectra was obtained, each of which records the rate at
which each of the elements present emits its spectrum for
that particular time interval. The photographic plate is
then processed and the intensities of the Cd, Tl, and Zn
line are determined from each spectrum. The intensity of
the lines is then plotted as the ordinate on semi-log
coordinate paper and time as the abscissa. Consecutive
points for each element are connected by straight lines.
The intensities of the three lines will be observed to
decrease and increase in somewhat the same manner until
the sample has burned for 60 seconds, at which time the
Cd and Zn lines appear much more intense and the Tl line
much less intense. The conclusion is that Tl is a satis-
factory internal standard for Cd and Zn as long as all
exposures are made during the first 60 seconds in which
the sample is burned. Internal standards are usually
chosen for a particular element as a consequence of
information obtained from such a time study.

Preparation of Standard Samples for Working Curve

A set of standards for Cd and Zn with internal stan-
dards added was weighed out and tamped into 1/4-inch high
purity graphite electrodes. Another similar set for Co,
Cr, Cu, Fe, Mn, Mo, Ni, and Sn was prepared. Fig. 3,

Group I shows the type of electrodes used for Cd and Zn, and Fig. 3, Group II, III shows the type used for the remaining elements.
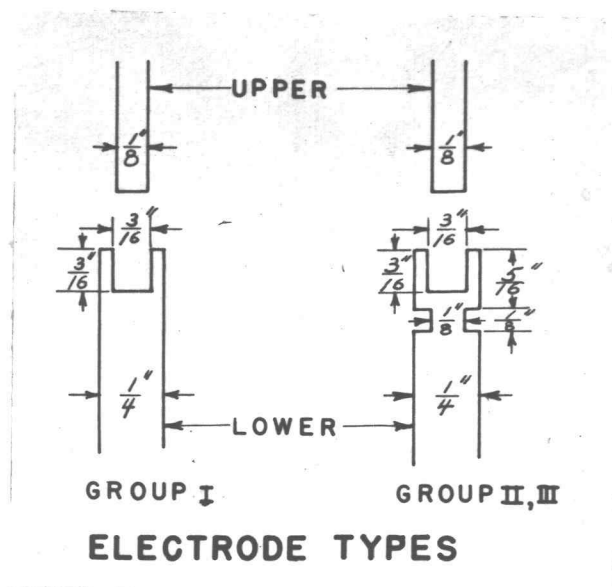

ELECTRODE TYPES

Fig. 3

The undercut electrode was chosen for Group II, III primarily because of the higher temperatures which may be obtained with this type of electrode. The undercut increases the temperature of the upper portion of the electrode because of two phenomena. First, the heat which is incident upon the upper face of the undercut is reflected back to the sample and arc column, and second, the constriction caused by the undercut reduces the area of the electrode through which conduction of heat to the water cooled electrodes takes place. Since it requires a relatively high temperature to volatilize the elements of Group III, this type of electrode was selected. The

elements of Group II are somewhat more volatile than the elements of Group III, but it was found convenient to use the same type of electrode for both groups.

Because of the high volatilities of Cd and Zn, it is desirable to use a much cooler burning electrode when analyzing for these elements. With the type of electrode selected for Group I, the Cd and Zn do not burn completely away until the sample has burned for 75 seconds. In an undercut electrode the Cd and Zn are completely burned away in the first 15 seconds of the burning cycle. Such short exposures are not desirable because of the difficulty of obtaining reproducible results. For further discussion of the uses of various types of electrodes, the reader is referred to Harvey (3, pp.335-340) or Ahrens (1, pp.48-50).

The samples were then arced and the resulting spectrograms processed.

Construction of Working Curves

Each photographic plate contains an iron spectrum. The purpose of this spectrum is to assist in determining the gamma of development of the plate and also to aid in alignment of unknown spectra against the known spectra on the master plate used for qualitative analysis. After determining gamma, one then converts per cent transmission readings into relative intensity values. The

procedures used are discussed later under photometry.
One then plots the ratio of intensity of analysis line to
intensity of internal standard line as the ordinate on
log-log coordinate paper and concentration of analysis
element as the abscissa. The resulting curve is called
the working curve for the analysis element and all subse-
quent intensity ratios for this element are referred to
this curve. Fig. 4 shows the wave-length used for
analysis of each element, and the element and wave-length
used as the internal standard in constructing the working
curves. The manner in which these curves are transferred
to the calculating board is described in a later section.

Elements	Wave Lengths	Internal Standards
Cd	3261.1	Tl 2767.9
Co	3453.5	Pd 3242.7
Cr	2986.5	Pd 3242.7
Cu	3247.5	Ga 2874.2
Fe	3020.6	Pd 3242.7
Mn	2576.1	Pd 3242.7
Mo	3132.6	Ga 2874.2
Ni	3101.6	Pd 3242.7
Sn	3175.0	Pd 3242.7
Zn	3345.0	Tl 2767.9

Spectral Lines Used In Constructing
Working Curves

Fig. 4

Correction of Working Curves

Fig. 5 shows working curves for Mo, Cu, and Mn. The
curve for Mo has been shifted one cycle to the left in

order to prevent it from crossing the Mn curve. For optimum accuracy these curves would all slope upward at an angle of 45°. For this particular base material, the emission factor, defined as the slope of the working curve, is somewhat less than unity (1, p.78). The intensity of the analysis line then varies according to the equation

$$I = KC^n$$

where I = intensity of analysis line

K = a constant

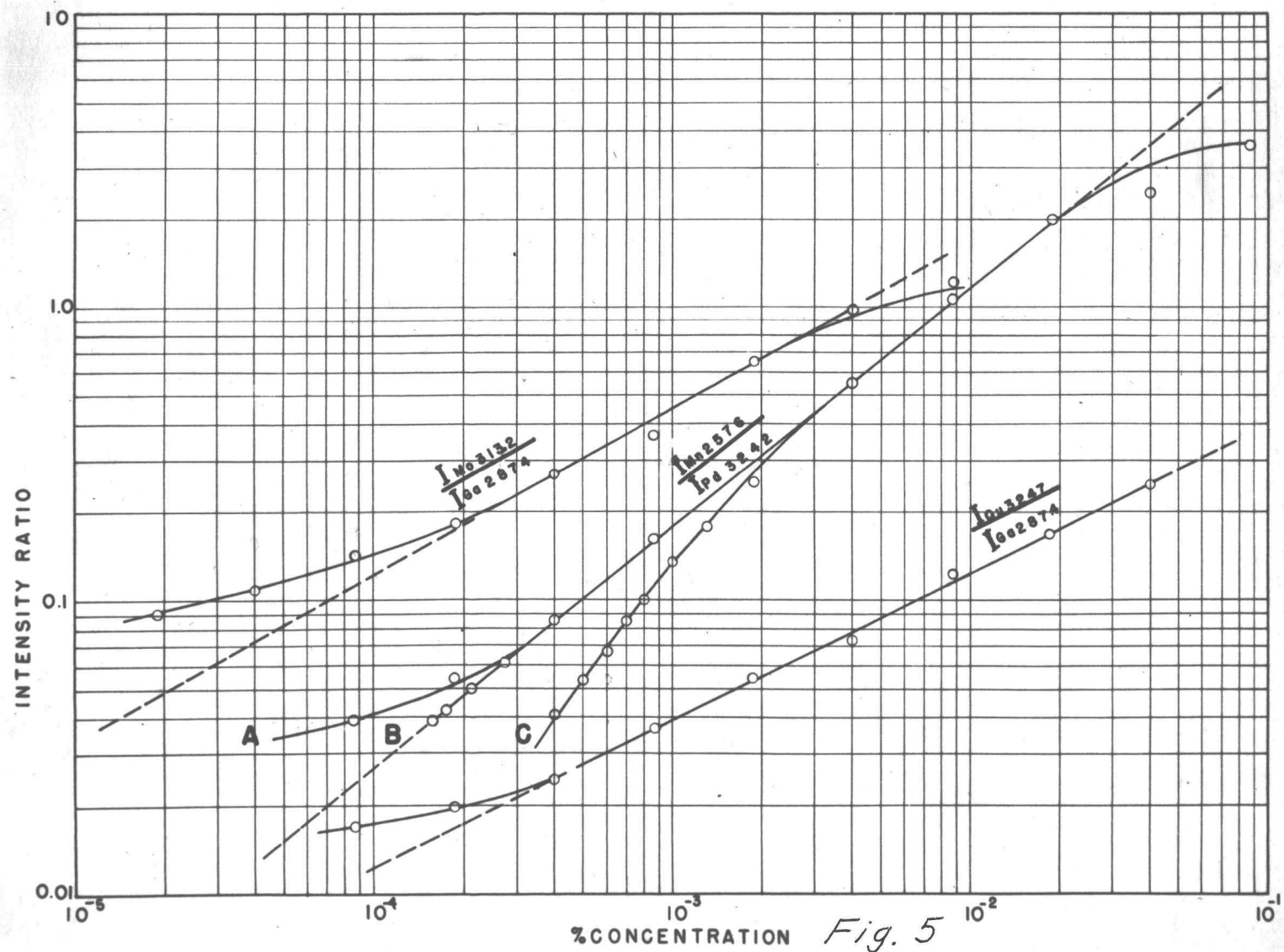C = concentration of analysis element

n = emission factor

or

$$\log I = \log K + n \log C$$

Therefore, with n<1 the slope of the curve log I vs n log C is less than unity. This situation is not serious but at the same time is not desirable. The author knows of no procedure and has found no reference for a method of increasing the slope.

It will be observed that all three curves of Fig. 5 depart from straight lines on both the low and the high concentration ends. The tapering off at the high concentration end is undoubtedly due to self-absorption of the analysis line (1, pp.29-32). The curve for Mn has been extrapolated to higher concentrations in order to obtain an estimate of the concentration of Mn for intensity

ratios greater than about 2.5. For these higher concentrations a less intense line should be used and a new curve plotted.

The tapering off of the curve on the low concentration end is due to residual impurities of the element in the base powder (5, pp.139-141). If it were not for the presence of this residual impurity, one would expect the curve to be linear down to the lowest concentration detectable. Curve A in Fig. 5 shows the uncorrected Mn curve. To correct this curve, one makes a guess at the concentration of the residual impurity and shifts the points on curve A toward higher concentrations (by the amount estimated) and plots a new curve. Curve C illustrates an over-corrected curve where the residual impurity was estimated to be 3 parts per million. Curve B has been corrected for 1 part per million and since this correction results in a straight line, it is assumed that this is the correct concentration of the residual impurity.

Fig. 5

$\frac{I_{Mo\,3132}}{I_{Ga\,2874}}$

$\frac{I_{Mn\,2576}}{I_{Pd\,3242}}$

$\frac{I_{Au\,3247}}{I_{Ga\,2874}}$

A

B

C

INTENSITY RATIO

%CONCENTRATION

18

SPECTROGRAPHIC PHOTOMETRY

Microphotometer Data

Adequate instructions for the operation of the Jarrell-Ash microphotometer are furnished with the instrument. Since the rotating sector was used to vary the exposures on all spectra, it is usually possible to select that portion of the spectral line for which the per cent transmission lies on the linear portion of the gamma curve. This portion usually lies in the region from 10% to 70% transmission.

For a low contrast emulsion such as SA-2, a background reading of 90 per cent transmission will represent about 10% of the intensity of a spectral line whose net transmission is 20%. The intensity of such a background is relatively small and may be neglected provided that both the analysis line and the internal standard line have nearly the same background intensity. Should one of the backgrounds above be considerably different from the other, a background correction should be made.

For each element of Group III the backgrounds may vary from 65% to 95%. One cannot neglect variations as great as this or backgrounds greater than 90%. Hence, corrections were made for all elements of this group. Variation in background is increased by higher burning

temperatures. No correction for background was made in constructing the working curves for Cd, Zn, Cu, and Mo. When background corrections are made the intensity of the line and background must first be determined. The intensity of the background is then subtracted from the intensity of the line. Under no conditions should one correct for background by subtracting the per cent transmission of background from the per cent transmission reading of the line as this is not a valid procedure (5, pp.135-139).

Construction of the Fan Scale Used on Calculating Board

In quantitative spectrographic analyses, it is necessary to convert microphotometer per cent transmission readings into relative intensity values. The usual manner of doing this is to construct a gamma curve on which log per cent transmission is plotted as ordinate and log relative intensity is plotted as abscissa. To convert per cent transmission into relative intensity, one merely records the abscissa corresponding to a given transmission reading.

There are two reasons why the above procedure of calculating relative intensities is unsatisfactory. First, the large number of conversions required for evaluating each photographic plate makes such a procedure very slow and tedious. Second, we would be assuming that we could develop all of our photographic plates to the same

gamma merely by controlling the processing conditions. We could overcome the second objection by constructing a family of gamma curves, but if the gamma of a plate did not exactly match the gamma of one of the family of curves, our problem would again be unsolved.

The fan scale as described below actually eliminates both of the above objections and, in fact, contains an infinite number of gamma curves.

The calculating board on which the fan scale is used is designed very similar to one produced by Jarrell-Ash Company (4). It was designed and constructed by Dr. Duis D. Bolinger and is half as large as the one made by Jarrell-Ash Company, but with equal accuracy. The fan scale is moved independently in the horizontal and vertical direction by rack and pinion motions for accurate settings.

The fan scale for Kodak Spectrum Analysis No. 2 photographic plates was constructed as follows. A rotating stepped sector was placed immediately in front of the spectrograph slit. The manner in which the light incident on the slit is varied is illustrated in Fig. 6.

The total amount of light through successive portions of the slit is proportional to the angles θ_1, θ_2, etc. The relative intensities of light passing through successive portions of the slit are proportional to the angles

θ_1, θ_2, etc. For this calibration problem a "Jaco"-65
rotating stepped sector was used. This sector is designed
with seven 1.5mm steps so that log θ_1/θ_2 = 0.2 or
log $\dfrac{I_1}{I_2}$ = 0.2 for each pair of successive steps. For this
step relation 2X2 cycle log-log paper with a 5-inch cycle
is very useful in plotting resulting data since each
relative intensity value is separated on the graph a dis-
tance of one inch and the relative intensity is so chosen
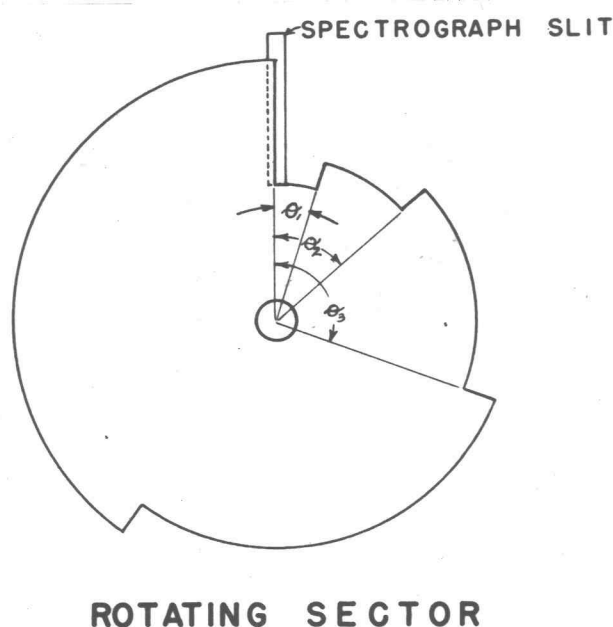that one value lies on the beginning of each cycle.

ROTATING SECTOR

Fig. 6

Because the rotating step sector has only seven
steps and use of a lesser number may be necessary because
of nonuniform illumination over the length of the spec-
trograph slit, the author made use of a method described
by Harvey (3, pp.73-76) in which a large number of points

may be obtained. The manner in which this was accomplished is shown in Fig. 7, page 24.

A smooth curve is drawn through the points obtained from the Fe 3083.75 line. If the intensities of the Fe 3134.11 line be multiplied by a factor of 0.28, the points will be shifted to the left to coincidence with the curve drawn for the Fe 3083.75 line. Similarly, multiplication of the intensities of the Fe 3153.2 line by a factor of 0.17 brings these intensity values to their proper position with respect to the Fe 3083.75 line. The results obtained indicate that the intermittency effect (3,p.63) is very small if present at all.

Since the spectrograph slit length was opened to 9mm in order to utilize as many of the rotating sector steps as possible, it was necessary to first determine whether or not the slit was being illuminated uniformly. Trial and error finally showed that if an alternating current arc source of 4800 volts and 2 amperes was used with iron electrodes separated 10mm, a very uniform slit illumination would result.

Three Kodak Spectrum Analysis No. 2 plates were exposed to the A.C. arc light source for 100 seconds and developed for $1\frac{1}{2}$, 3, 10 minutes in Kodak D-19 developer at 20°C. The resulting gamma curves had gamma values of 0.93, 1.10, 1.25, respectively.
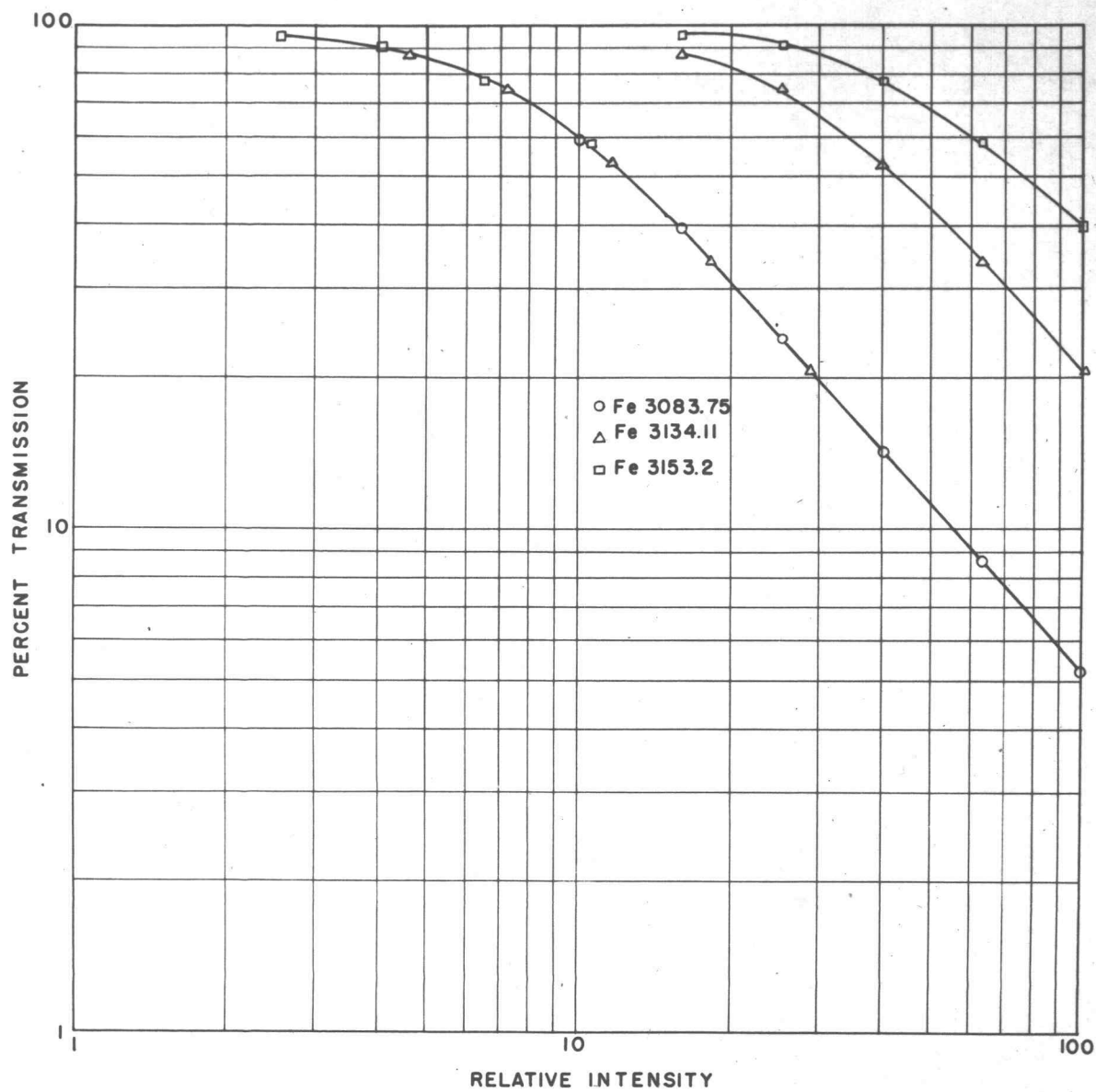
Fig. 7

Each gamma curve was plotted on a separate sheet of graph paper. The three curves were then placed one on top of another and placed on a viewing box so that all three curves could be seen simultaneously. The curves were then adjusted by moving each graph in a horizontal direction until all three curves intersected at the point where their transmission values were 10%. This intersection point is arbitrary. Fig. 8 illustrates how the fan scale is obtained from these three gamma curves.

The horizontal line whose gamma value is taken to be 0.95 is located at a convenient distance below the relative intensity scale of the gamma curves. The horizontal line whose gamma value is 1.25 is located about three inches below the line for which gamma is 0.95. This separation is arbitrary. Next, the horizontal line representing the 90% transmission line is extended so as to cross all three gamma curves. The 3.5% transmission line is similarly extended to intersect the gamma curves. Through the points of intersection of the 90% and 3.5% transmission lines and the 0.95 and 1.25 gamma curves, vertical lines are drawn and extended until they intersect the horizontal lines corresponding to the same gamma value. The points on the horizontal gamma lines corresponding to the same transmission values are then connected by oblique lines as shown. The whole procedure of projecting transmission values from the gamma curves to the

fan scale is repeated until a representative number of transmission readings is projected onto the fan scale. The proper transmission reading is then recorded on top of the fan scale. If the oblique lines are extended downward, they will all intersect at a point as shown in Fig. 8. This point corresponds to a gamma value of infinity.

The gamma value 1.1 is located on the fan scale at that height at which the vertical line from the corresponding gamma curve intersects with its corresponding transmission value on the fan scale. Fig. 9, page 28, is a photograph of a completed fan scale.

CONSTRUCTION OF FAN SCALE   Fig. 8

WORKING CURVE STRIPS

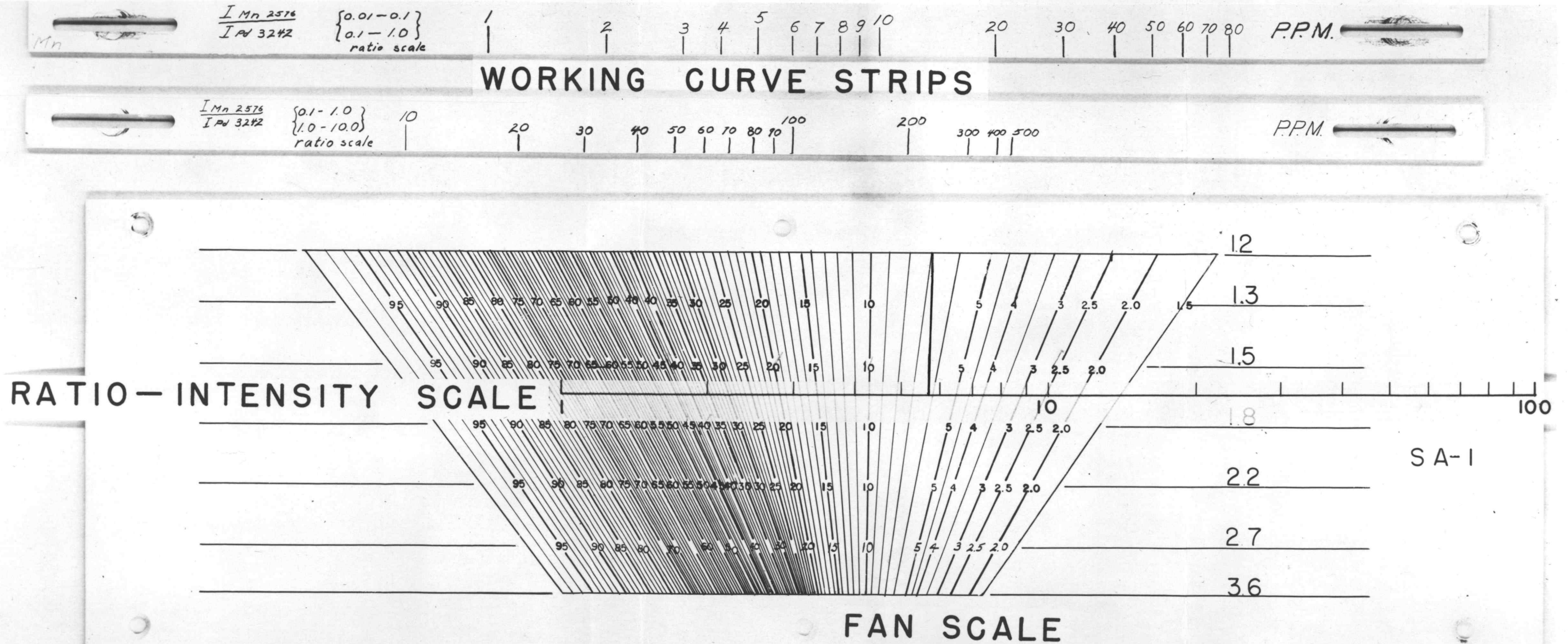RATIO — INTENSITY SCALE

FAN SCALE
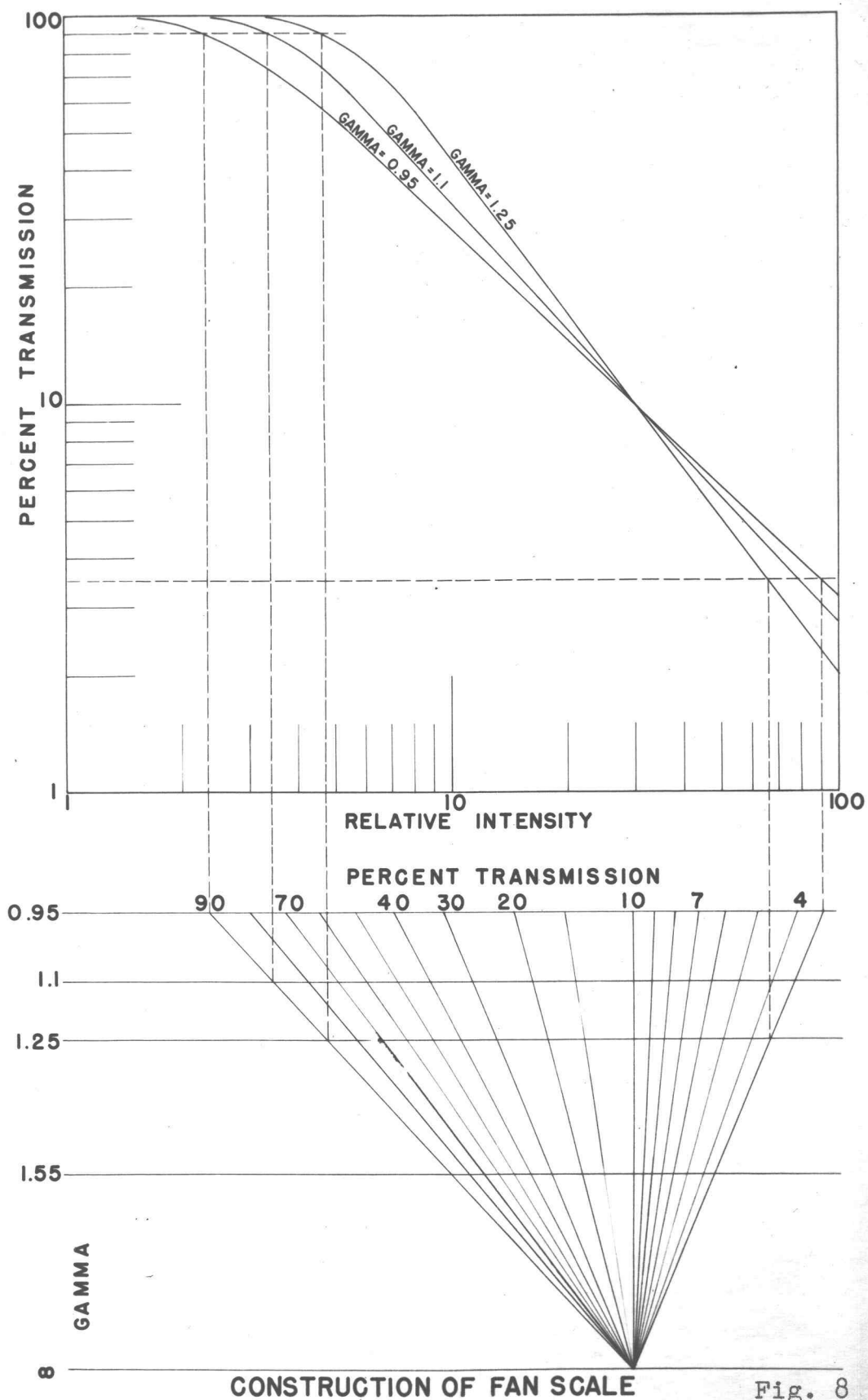
Fig. 9

Use of the Calculating Board

1. Calculating Gamma. In using the calculating
board to determine gamma, the author made use of the known
relative intensities of a few iron lines (6, p.33).
Listed below are several such lines along with their
relative intensities. To determine gamma, it is first
necessary to find the per cent transmission readings of
two of the iron lines listed below.

Iron Lines

Wave Length	Relative Intensity
3163.9	0.19
3168.9	0.31
3165.0	0.42
3165.9	0.67
3166.4	1.00
3175.4	2.00
3180.2	3.63
3196.9	6.30

Suppose for example that the Fe 3166.4 line has a trans-
mission reading of 80% and the Fe 3196.9 line has a
transmission reading of 20%. The fan scale is then moved
in a horizontal direction until the 20% transmission
reading on the fan scale lies directly below 6.30 on the
intensity scale, 6.3 being the relative intensity of the
Fe 3196.9 to the Fe 3166.4 line. The fan scale is then
moved in both the horizontal and vertical directions
(always keeping 20% transmission directly under intensity
6.30) until the 80% transmission reading is directly
below intensity 1.00 (the intensity of the Fe 3166.4 line).

The fan scale is now set for the proper gamma.

2. <u>Converting</u> <u>Per</u> <u>Cent</u> <u>Transmission</u> <u>Readings</u> <u>Into</u> <u>Relative</u> <u>Intensities</u>. Since the intensities as determined by the gamma curve are relative intensities, the intensity ratios obtained from the calculating board do not depend upon the horizontal position of the fan scale. Once having determined gamma, one has only to read the intensity scale immediately above the particular per cent transmission reading in order to obtain the corresponding intensity.

Reference to Fig. 9 illustrates the manner in which this is accomplished. Suppose for example that the gamma value for the plate was 1.2 and it is desired to find the relative intensity corresponding to a transmission reading of 7.0%. From the 7.0% transmission reading on the gamma 1.2 level one projects vertically downward to intersect the Ratio-Intensity Scale at 5.8. Thus 5.8 is the relative intensity corresponding to 7.0% transmission for this gamma value. Since this is a relative intensity, its value could equally as well be 58.0, 580, 0.58, etc. by assigning other decimal values to the Ratio-Intensity Scale. Here we have used the Ratio-Intensity Scale as an intensity scale. (For purposes of converting intensity ratios into concentrations, the Ratio-Intensity Scale is used as a ratio scale. The proper ratios to be used with each working curve strip are recorded on that strip as

ratio scales. Thus the lower strip indicates that intensity ratios from 0.1 to 1.0 and 1.0 to 10.0 are to be referred to this strip. The Ratio-Intensity Scale is labeled from 1 to 100. This designation is arbitrary. It could just as well be labeled from 0.01 to 1.0, etc. The values assigned to the Ratio-Intensity Scale must agree with the values labeled "ratio scale" on the working curve strips.)

3. <u>Shifting Working Curves to Proper Position</u>. In Fig. 9 the working curve strips for Mn in concentrations from 1 to 80 parts per million and from 10 to 500 parts per million are pictured. Reference to the working curve for Mn in Fig. 5, page 18 will show that corresponding to an intensity ratio of 1.0, the concentration of Mn is 0.0080% or 80 parts per million (PPM). Using the lower working curve one will notice that the mark designating 80 PPM does not lie directly above 1.0 on the Ratio-Intensity Scale. For this case we choose ratios of 0.1 to 10.0. The working curve strip must now be shifted so that the line designating 80 PPM lies directly above 1.0 on the Ratio-Intensity Scale. The working curve strip could be shifted directly to the proper horizontal position but in practice the following procedure is followed. In order to help eliminate any extraneous spectrographic variables, four spectra of standard samples are recorded

on each plate. For this purpose two electrodes are pre-
pared for each of two different standards. The intensity
ratios are calculated and the working curves shifted in
the horizontal direction until the two different known
concentrations best coincide with their respective
intensity ratios. The working curve strips are now in
their proper positions and all intensity ratios for Mn
from this particular plate may be converted into concen-
trations without moving the strips again.

DETAILED PROCEDURE FOR ANALYSIS

Sample

>7mg internal standards plus 38.0mg sample
>
>Grind together in agate mortar and tamp sample in cup in quarter-inch high purity graphite electrode

Electrodes (See Fig. 3, page 13)

>Upper electrode (negative)
>
>>1/8-inch high purity graphite rod
>
>Lower electrode (positive)
>
>>Group I. 1/4-inch high purity graphite rod drilled out with a 3/16-inch drill to depth of 3/16 inch
>>
>>Group II, III. Same as for Group I electrode except lower electrode is undercut

Optical system

>Arc stand at 63.2cm
>
>67CQ condensing lens at 54.2cm
>
>Rotating sector at 30.2cm full speed
>
>Slit width 30 microns
>
>Slit height 3.0 millimeters
>
>Spectral region 2350-4100A
>
>Steps No. 3, 4 of "JACO"-65 rotating sector rotating at full speed

Emulsion

    Spectrum Analysis No. 2 plate

Excitation

    D.C. arc at 20.0 amperes for sample, arc gap 3mm

    4800 volt A.C. arc at 2.0 amperes for Fe spectrum

Exposure

    Two identical consecutive arcings for each electrode,

    pre-arcing for 10 seconds and exposing for 50

    seconds - first exposure for elements of Group II,

    second exposure for elements of Group III

    60 seconds exposure for Fe spectrum

Development

    3 minutes in Kodak D-19 developer at 20°C.

    Agitate constantly

    Place in 1% acetic acid bath for 20 seconds

    Place in hypo for 20 minutes

    Wash in tap water for one hour

Photometry

    Microphotometer slit width 0.20mm, slit height 5.0mm

    No background correction for Zn, Cd, Cu, Mo

    Background correction necessary for Co, Cr, Mn, Mo,

    Ni, Sn

    Read transmission of spectral lines as listed in

    Fig. 4, page 15

    Set 100% transmission on clear film

SPECTROGRAPHIC RESULTS

Standard Deviation

Because of the many variables involved in spectrographic analysis, an estimate of the accuracy of the method at this time would be premature. The reproducibility of the method can be calculated however, and the results expressed in terms of standard deviation (1, p.105-108). By standard deviation we mean $S = \sqrt{\dfrac{\sum d^2}{n-1}}$ where d is the deviation and n is the number of determinations. Listed below are intensity ratios for ten samples from which the standard deviation for the analysis of Mo was calculated.

$\dfrac{I_{Mo3132.6}}{I_{Ga2874.2}}$	Deviation	(Deviation)^2
0.23	-.004	.00002
0.30	.066	.00435
0.27	.036	.00130
0.24	.006	.00004
0.26	.026	.00068
0.17	-.064	.00410
0.21	-.024	.00058
0.25	.016	.00026
0.20	-.034	.00118
0.21	-.024	.00058
Average 0.234	.030	.01309

Average Deviation = .030 (13%)

Standard Deviation = .038 (16%)

From these data a standard deviation of 16% was obtained. Since the working curve for Mo has a slope of somewhat less than 45°, the standard deviation for concentration of Mo would be slightly larger than 16%. The reproducibility of this method for Mo would generally be considered fair (1, p.85). Standard deviation for the remaining elements has not been calculated as yet.

Comparison of Chemical Analysis with Spectrographic Analysis for Three Representative Samples

Fig. 10 below lists the results obtained by both chemical and spectrographic analysis of three typical samples.

Sample Identification	Chemical Analysis		Spectrographic Analysis	
	Element	Concentration %	Element	Concentration %
No. 11440 Cow Clover Prairie City, Oregon	Cu	0.0034	Cu	0.0037
	Fe	0.097	Fe	0.055
	Mn	0.052	Mn	0.055
	Mo	0.0040	Mo	0.0040
No. 10398 Tideland Pasture Astoria, Oregon	Cu	0.0084	Cu	0.0064
	Fe	0.32	Fe	0.08
	Mn	0.165	Mn	0.0072
	Mo	0.0030	Mo	0.0024
No. 10400 Alta fescue straw Corvallis area	Cu	0.0017	Cu	0.0017
	Fe	0.081	Fe	0.0060
	Mn	0.076	Mn	0.0038
	Mo	0.0008	Mo	0.0003

Comparison of Spectrographic Analysis with Chemical Analysis of Selected Plant Ash Samples

Fig. 10

These samples were chosen for comparison primarily because
of the variation in concentration of trace elements. The
agreement of the two types of analyses for Cu and Mo is
quite good on all three samples. On the other hand, the
agreement for Fe and Mn varies from good to very poor.
The best over-all agreement is obtained from sample
No. 11440. Further investigation may show that the chemi-
cal composition of this sample more closely approaches
that of the synthetic plant ash used in preparation of the
working curves than do the other two samples. The agree-
ment for Fe and Mn is not satisfactory, and must be
improved before the spectrographic analysis will be of
any real value.

Possible Sources of Error

Let us assume that the results obtained by chemical
analysis are correct. Doing this we have but one choice
and that is to assume that the emission of the Fe and Mn
spectra are being retarded by some agent contained in the
sample itself. This is evident from the low concentra-
tions obtained for sample No. 10398 and No. 10400.
Whether this retardation of the Fe and Mn spectra is
caused by the presence of other trace elements in rela-
tively high concentrations or a high variation in the
major constituents of the sample is not known at present.
This is probably the largest source of error. Possible

sources of error in general are:

1. Wandering of image of arc on and off of the spectrograph slit;

2. Errors in weighing out samples and internal standards;

3. Inhomogeneity of sample and internal standards;

4. Error in determining gamma of development;

5. Error in reading per cent transmission of spectral lines; and

6. Human errors in reading scales.

Suggestions for Improving Method

The effects caused by a variation of the major constituents of the plant ash should be investigated first. It is believed that this variable will account for the low values obtained for Fe and Mn. If this proves to be the case, then it could probably be corrected by using information obtained from a detailed time study. The procedure would be to investigate the emission of the Fe and Mn spectra as a function of time for a series of samples whose major constituents vary from sample to sample. From this study one could obtain information which would indicate the proper pre-arcing and exposure times to use for the particular composition sample being analyzed.

Because of the presence of band spectra in the vicinity of the Co 3453.5 line, it has not been possible to detect Co in amounts of less than 0.001%. If the band

spectra could be partially eliminated by one of the methods suggested by Ahrens (1, p.148-149), then the lower limit of detectability could probably be extended to about 0.0001%.

Fig. 11 below shows the lower limits of detectability of the elements by this method.

Elements	Lowest Limit of Detectability as:	
	% in Sample	PPM in Dry Forage
Cd	0.03	30.0
Co	0.001	1.0
Cr	0.001	1.0
Cu	0.0001	0.1
Fe	0.001	1.0
Mn	0.0002	0.20
Mo	0.0004	0.40
Ni	0.001	1.0
Sn	0.001	1.0
Zn	0.03	30.0

Limits of Detectability by Direct Arcing Method

Fig. 11

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