Relative Sensitivities of Elements in a Spark-Source Mass Spectrograph[*1]

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For the quantitative analysis of solids by spark-source mass spectrography, at least two fundamental problems must be studied. One of them concerns a calibration method to obtain the relative ion intensity from the densities of mass lines recorded on a photographic plate. The other concerns the relative sensitivities of elements in a mass spectrograph with a pulsed radio-frequency spark ion source, which has been generally used as the most suitable ion source for the trace analysis of solids since it was first applied to mass spectroscopy by Dempster.[1,2] The sensitivity is a function of both the darkening rate of a photographic plate and the ion production rate from a solid by a spark discharge between two sample electrodes. Therefore, the sensitivity is not only necessary as an analytical constant in quantitative mass spectrography but also very important for the study of the mechanism of ion production by spark discharges in a vacuum. However, relatively little work has been done on the sensitivity,[3,4] and no study has previously been made of the ion production rate using photographic detection.

Thus, a study of the calibration method has been made in this laboratory, and the findings partly published in a preceding paper.[5] For the present work, five kinds of calibration methods have been investigated by applying them to isotopic analyses of magnesium, copper and zinc. The relative sensitivities have been determined for eleven elements contained in several standard samples using the calibration methods mentioned above, and the constancy of the sensitivity to changes in bulk concentration of the element has been examined. The relative ion production rates have also been determined from the above sensitivities with a correction for the darkening rate. In addition, the reproducibility of the relative ion intensities detected with several plates in many exposure stages has been studied for many pairs of isotopes and pairs of different elements, in order to examine whether the relative ion yields obtained from the spark ion source are always constant for all elements contained in the sample electrodes. Finally, a discussion will be given on the general applicability of the sensitivity as the analytical constant.

Apparatus

The Mattauch-Herzog-type double-focusing mass spectrograph used in this work was constructed in this laboratory in collaboration with the Mitsubishi Elec. Mfg. Co. Since details of the instrument have been reported elsewhere,[6] only an outline and the operating conditions employed will be given here. The ion source used was a Dempster-type vacuum spark ion source; the spark voltage applied between two sample electrodes, each about 1 mm. in diameter and 1 cm. in length, was approximately 30 kV., supplied from a 1 Mc./sec. radio-frequency oscillator with pulses about 200 μsec. long at a repetition rate of 60 c./sec. Ions produced under a vacuum of about 5×10^{-6} Torr were accelerated with 15 kV. through the slit system, inclusive of a 0.21 mm. defining slit. Of the ions passing through the energy selector with a mean radius of 150 mm., about 42 per cent enter the magnetic field, and the rest are collected by the beam-monitor electrode which is situated directly behind a selector slit and which is shielded from the field of the radio-frequency used for the spark source.

Individual ions resolved by the mass analyzer were detected by a 3 cm. × 15 cm. Ilford Q2 plate, which covers a mass range of 10 : 1 in a single exposure. Moreover, eleven exposures can be recorded on the plate without loss of vacuum. The amount of each exposure was determined by the total ion current arriving at the beam-monitor during the exposure. For this purpose, a vibrating-reed electrometer manufactured by the Electronic Instrument Ltd. was used in combination with a 500 pF polystyrene condenser. The exposed plate was developed by an Ilford ID-19 developer continuously agitated by hand at temperatures 20±1°C for exactly 5 min., then it was fixed by Fujifix for about 3 min., washed, and dried. For the purpose

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1) A. J. Dempster, *Nature*, 135, 542 (1935).

2) A. J. Dempster, *Rev. Sci. Instr.*, 7, 46 (1936).

3) A. J. Dempster, MDDC-370, United States Atomic Energy Commission, Oak Ridge (1946).

4) R. D. Craig, G. A. Errock and J. D. Waldron, "Advances in Mass Spectrometry," Ed. by J. D. Waldron, Pergamon Press, London (1959), p. 136.

5) K. Kodera, T. Makita, J. Kai, S. Fukuda and H. Kawano, *Mass Spectroscopy* (*Shitsuryô Bunseki*), 9, 105 (1961).

6) M. Goto and J. Kai, *Mitsubishi Denki Laboratory Reports*, 1, 51 (1960).

of determining the optical densities of the mass lines, about 2 mm. long and about 0.2 to 0.8 mm. wide on a photographic plate, each spectrum, magnified about 9 times, was scanned through a 0.20 mm. × 3 mm. slit and was registered by a microphotometer with a recorder manufactured by the Rigaku-Denki Co., Ltd.

Experimental Method

Calibration Curve.—*Expression of Density.*—For quantitative analysis by photometry, it is necessary to make a calibration curve which shows the relation between the density of each mass line and its corresponding exposure. It is desirable that the curve has a linear portion over a wider range of exposure. Thus, various methods have been studied to get useful calibration curves from a series of the mass lines of a certain ion recorded by different exposures on the same plate. Among the methods studied, five have been employed here to express the "density" of each mass line:

$$D_1 = \log L_0/L$$

$$D_2 = \log(L_0 - L)/L_0$$

$$D_3 = (L_0 - L)/L_0$$

$$D_4 = \log(L_0 - L)/L$$

$$D_5 = (L_0 - L)/L$$

where L_0 and L are the intensities of the incident and the transmitted light in arbitrary units respectively. Examples of the calibration curves using these density expressions are shown in Fig. 1, at the top of which the peak height, $L_0 - L$ (i. e., the intensity of the absorbed light) is plotted in per cent of L_0 in order to show the range which corresponds to the linear portion of each calibration curve.

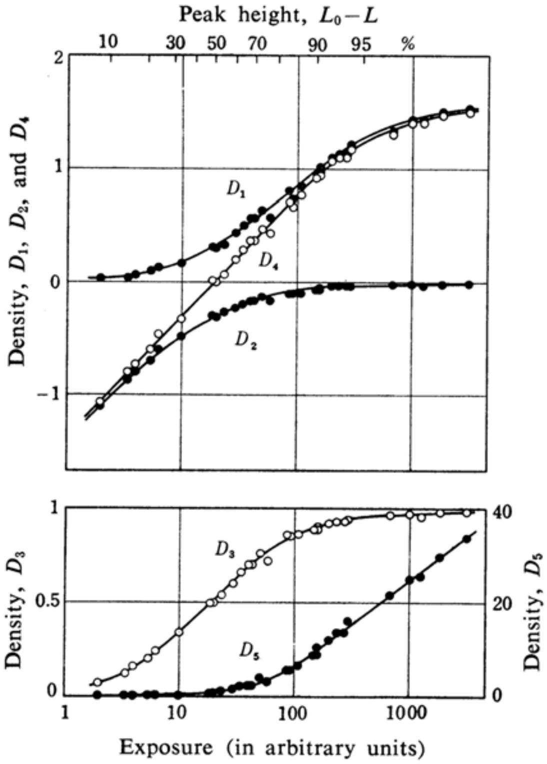

Fig. 1. Examples of the five kinds of calibration curves obtained for zinc isotopes recorded on an Ilford Q2 plate using the different expressions of density. In order to utilize many data points, $r \times Q$ instead of Q was employed as the "exposure", where r and Q are the known relative abundance of each isotope of zinc and the measured value of the integrated monitor current in each exposure stage, respectively.

The D_1 expression is the equation of Lambert-Beer's law; it is generally used as an expression of density in mass spectrography. However, in the calibration curve where D_1 is plotted against the logarithm of exposure, more than one-half of the series of mass lines obtained for a certain ion in several exposures are, on the average, unavailable for the calibration only because they are out of the linear portion of the density curve, as may be seen in Fig. 1. For this reason, the usable D_1-curves for all ionic species under investigation can not always be obtained from an exposure range covered by up to eleven exposures. In the other curves, however, using D_2, D_3, D_4, or D_5, it is possible to utilize even those mass lines which are unavailable for the calibration in the D_1-curve because they are too intense or too weak to fall in the linear part. Especially in the D_2- or D_4-curve, any weakline is available so long as it exceeds the noise level around it to a certain degree. Therefore, short exposures less than one-tenth of those necessary in the D_1-curve are sufficient here to get useful curves. Thus, employing the D_2- or D_4-expression is more advantageous when long exposures are undesirable or have produced only weak lines for some of the ions to be studied. Some examples of the D_4-curves obtained from a single Q2 plate, subjected to ten short exposures graded with a factor of about 2 between adjacent stages, is shown in Fig. 2. In the examples no useful curve can be obtained for zinc and manganese if the D_1- or D_5-expression is employed. In the D_5-curve, on the other hand, only intense lines are usable, so this curve is available for the determination of those major elements which from nearly saturated lines. The D_3-curve is appropriate to some of the lines that are unavailable in the D_1- or D_2-curve because they are too weak or too intense respectively. The characteristics of the different expressions of density described above are listed briefly in Table I.

TABLE I. CHARACTERISTICS OF EACH CALIBRATION CURVE, D_n VS. log *Exposure*, OBTAINED FOR AN ILFORD Q2 PLATE (EMULSION NUMBER : S 3399)

The "asymptote" indicates the maximum or the minimum density level to which a calibration curve approaches asymptotically, as the amount of exposure increases or decreases respectively. The "useful range" means (A) the range of peak height in per cent of L_0 or (B) that of the density value which corresponds to the linear part of the curve (cf. Fig. 1). Of the values shown in the second and the third columns, only those with an asterisk are dependent on the characteristics of a photographic plate and on the conditions of development employed.

Density expression	Asymptote	Useful range	Remarks
D_1	$D\approx 1.6^*$ $D=0$	(A) $50^* \sim 90^*\%$ (B) $0.3^* \sim 1.0^*$	Useless for low peaks. Long exposure is necessary.
D_2	$D=0$	(A) $0 \sim 40^*\%$ (B) $-\infty \sim -0.4^*$	Applicable to low peaks only. The shortest exposure among the five is sufficient.
D_3	$D=1.0$ $D=0$	(A) $20^* \sim 80^*\%$ (B) $0.2^* \sim 0.8^*$	Applicable to intermediate peaks.
D_4	$D\approx 1.6^*$	(A) $0 \sim 90^*\%$ (B) $-\infty \sim 1.0^*$	Applicable from low to high peaks. The linear part is the longest among the five.
D_5	$D=0$	(A) $80^* \sim 100\%$ (B) $4^* \sim \infty$	Applicable to high peaks only. The longest exposure among the five is necessary.

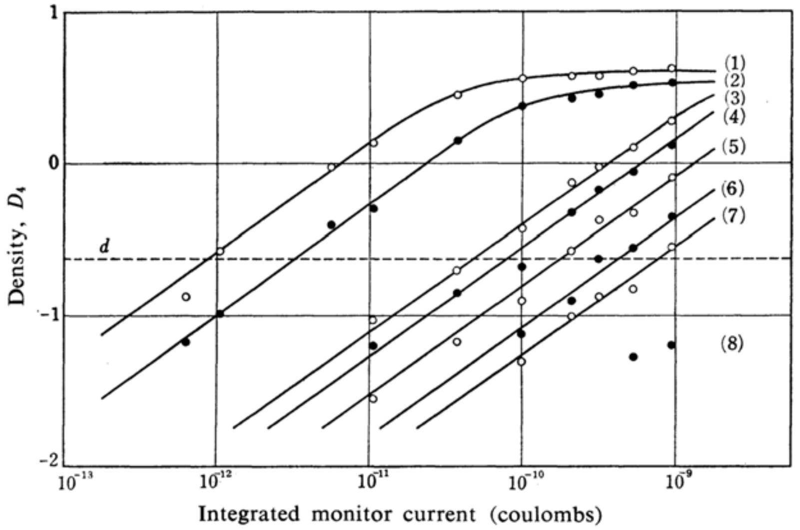

Fig. 2. An example of the calibration graph obtained for the samele S-3 from a Q2 plate using the D_4-expression in ordinate. The integrated monitor current of 10^{-9} coulombs corresponded to an exposure of about 3 min.

(1) : $^{26}Mg^+$ (2) : $^{27}Al^+$ (3) : $^{64}Zn^+$ (4) : $^{66}Zn^+$
(5) : $^{68}Zn^+$ (6) : $^{55}Mn^+$ (7) : $^{67}Zn^+$ (8) : $^{70}Zn^+$

Determination of Exposure.—In order to determine the amount of the "exposure" as a measure of the relative ion intensity corresponding to each line density, several methods have been utilized. One of them is Mattauch-Ewald's method, which uses as internal standards the known relative abundances of the isotopes of an element.[7-10] Therefore, its application is generally confined to those samples which contain in a moderate concentration such an element as has several isotopes with a suitable distribution of the relative abundance. As another method, the exposure time is employed.[11,12] However, in many cases the true amount of exposure can not be obtained from the exposure time without making an appropriate correction,[12] because it

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[7] J. Mattauch and H. Ewald, *Naturwiss.*, **31**, 487 (1943).
[8] J. Mattauch and H. Ewald, *Z. Phys.*, **122**, 314 (1944).
[9] H. Ewald, ibid., **122**, 487 (1944).
[10] J. Mattauch and H. Scheld, *Z. Naturforsch.*, **3a**, 105 (1948).
[11] N. B. Hannay and A. J. Ahearn, *Anal. Chem.*, **26**, 1056 (1954).
[12] N. Sasaki and J. Kai, *Mass Spectroscopy* (*Shitsuryô Bunseki*), **7**, 64 (1959).

TABLE II. ABUNDANCE RATIO OF COPPER ISOTOPES MEASURED BY THE FIVE KINDS OF CALIBRATION CURVES (D_n vs. $\log Q$), AND COMPARISON OF THE PRESENT MEASUREMENTS WITH PUBLISHED ONES OBTAINED BY PHOTOMETRY OR ELECTROMETRY USING SEVERAL IONIZATION METHODS

In square brackets are given the values corrected by Hess, et al.15)

Present work

Expression of density	Number of measurements	^{63}Cu/^{65}Cu
D_1	(A) 19	2.27±0.31
	(B) 4	2.14±0.07
D_2	(A) 13	2.16±0.26
	(B) 6	2.21±0.20
D_3	(A) 14	2.20±0.18
	(B) 7	2.25±0.26
D_4	(A) 14	2.22±0.26
	(B) 8	2.13±0.23
D_5	(A) 16	2.18±0.24
	(B) *1	

Reference

Methods of detection and ionization	Workers		^{63}Cu/^{65}Cu
Photometry*2 R. F. Spark	Ewald	9)	2.330±0.032 [2.163]
Photometry*2 R. F. Spark	Duckworth, Hogg	16)	2.277±0.017 [2.092]
Electrometry R. F. Spark	Dempster	17)*3	2.230±0.030
Electrometry Electron impact	White, Cameron	18)	2.220±0.020
Electrometry R. F. Spark	Sommer, Hipple	19)	2.220±0.027
Electrometry Ion impact	White, Sheffield, Rourke	20)	2.25±0.02

*1 Of the Cu$^+$ peaks obtained from eight plates using the sample B, none was available for the D_5-curve.

*2 Mattauch-Ewald's method was employed.

*3 Cited from Ref. 18.

is very difficult to keep spark discharges constant throughout all the exposures given to a plate, and much more so from plate to plate or from sample to sample. On the other hand, a monitor-current integration method[4,5,13] is free from the disadvantages mentioned above; i.e., no internal standard is necessary for making a calibration curve, and the error due to fluctuations of the total ion amount produced per sec. by spark discharges is avoidable because the integrated monitor current, Q, can be regarded as always proportional to any individual ion amount focused on a plate in any exposure. Therefore, this monitor method was employed, although the disturbance from the field of the R. F. current for spark discharges had to be shielded.

Isotopic Analysis for Testing the Methods.— For testing the usefulness of each D_n-curve for mass-spectrographic measurements, some isotopic analyses were tried using several samples. Each abundance ratio of the isotopes was calculated from the following equation:

$$r_i/r_j=(q_j/q_i)(m_i/m_j)^{1/2} \qquad (1)$$

where r_i and r_i are the abundances of the isotopes i and j respectively, q_i and q_j are the integrated monitor currents required for the line densities of i and j respectively to be at the same value, d, which is chosen so as to be on the linear part of the curves, as is shown in Fig. 2, and m_i and m_j are the masses of the isotopes i and j respectively. $(m_i/m_j)^{1/2}$ is the correction factor for the line widths,[14] needed because they vary in proportion to the square root of the mass in the Mattauch-Herzog arrangement.

The results obtained for copper are listed in Table II, where the ions studied are monatomic positive ions originating from two different samples, A and B, which contain about 90 and 1 weight per cent of copper respectively. As Table II shows, the mean values obtained by means of these calibration methods agree with one another rather well, and they also compare favorably with others referred to there. Therefore, the density expressions, D_2, D_3, D_4 and D_5, can be regarded as reliable as D_1. On the other hand, the standard deviations of the values measured with the five methods are about 10 times as large as those by Ewald[9] and Duckworth and Hogg.[16] This seems mainly due to the difference in calibration method. As the abscissa component of a calibration graph, the known relative abundance of the isotopes of a suitable element (zinc, for instance) has been taken, so that every value in the abscissa is free from erratic fluctuations.

The results obtained for magnesium and zinc are also in fair agreement with the referred values, as is shown in Tables III and IV respectively, where they have been calculated from those individually measured values which

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13) J. G. Gorman, E. J. Jones and J. A. Hipple, *Anal. Chem.*, **23**, 438 (1951).

14) H. Lichtblau and J. Mattauch, *Z. Phys.*, **117**, 502 (1941).

15) D. C. Hess, Jr., M. G. Inghram and R. J. Hayden, *Phys. Rev.*, **74**, 1531 (1948).

16) H. E. Duckworth and B. G. Hogg, ibid., **71**, 212 (1947).

17) A. J. Dempster, Report for February, CP-3445 (1946).

18) J. R. White and A. E. Cameron, *Phys. Rev.*, **74**, 991 (1948).

19) H. Sommer and J. A. Hipple, ibid., **83**, 229 (1951).

20) F. A. White, J. C. Sheffield and F. M. Rourke, *J. Appl. Phys.*, **33**, 2915 (1962).

TABLE III. ISOTOPIC ANALYSIS OF MAGNESIUM

The author's data have been obtained from 6 measurements.

Detection method	Mass number 24	25	26	Reference
Photometry	79.9±1.5%	9.1±0.5	11.0±0.9	Present work
Electrometry	77.4	11.5	11.1	Dempster 21)
Electrometry	78.60±0.13	10.11±0.05	11.29±0.08	White, Cameron 18)
Electrometry	78.8±0.2	10.15±0.1	11.06±0.1	White, Collins, Rourke 22)

TABLE IV. RELATIVE ABUNDANCE OF ZINC ISOTOPES OBTAINED FROM TWO DIFFERENT SAMPLES, AND COMPARISON WITH PUBLISHED VALUES

In the works A and B, zinc is contained about 2 and 95 weight per cent in the samples used, and the numbers of measurements are 21 and 20 respectively.

Detection method	Mass number 64	66	67	68	70	Reference
Photometry	47.9% ±5.2	28.0 ±3.4	4.3 ±1.1	19.0 ±3.8	0.8 ±0.2	Present work (A)
Photometry	48.3 ±3.4	27.8 ±2.2	4.9 ±1.7	18.3 ±2.3	0.7 ±0.3	Present work (B)
Photometry	50.4	27.2	4.2	17.8	0.4	Aston 23)
Electrometry	50.9	27.3	3.9	17.4	0.5	Nier 24)
Electrometry	48.89	27.81	4.11	18.56	0.62	Hess, Inghram, Hayden 25)*
Electrometry	48.89	27.81	4.07	18.61	0.620	Leland, Nier 26)
Electrometry	48.89 48.90	27.82 27.82	4.14 4.17	18.54 18.48	0.617 0.623	Hess, Inghram, Hayden 15)
Electrometry	49.77	27.19	4.09	18.54	0.41	Okamoto et al. 27)

* Cited from Ref. 28.

were obtained by using the most suitable calibration method among the five according to the densities of the isotopic lines to be studied. In the magnesium analysis, the sample used contains more than 90 weight per cent of magnesium, so that the intensities of the C_2^+, C_2H^+ and $C_2H_2^+$ ions, even if they exist, may be negligibly small compared with those of the magnesium ions.

From these results it seems reasonable to conclude that a mean value of the measurements obtained by any of the five calibration methods is as accurate as that by the electrometry, although good reproducibility has not yet been obtained in the present work.

The Determination of Relative Sensitivity.— If the ion intensity, I_X, of an element, X, which forms a line with a density, d, on a plate is expressed in arbitrary units by the following equation:

$$I_X = m_i^{1/2}/q_i \times r_i \tag{2}$$

where i is one of the isotopes of X and where every isotope is assumed, in a manner similar to that in Eq. 1, to have the same effect on photographic darkening, the relative sensitivity, S_X, of X will be given as:

$$S_X = S_R(\bar{I}_X/C_X)/(\bar{I}_R/C_R) \tag{3}$$

where S_R is that of the element, R, adopted as a reference, $\bar{I}$ is the arithmetic average of the I's obtained for all or some isotopes of the element, C is the atomic concentration of each element contained in a sample of known chemical composition, and S is assumed to be independent of C. The samples used are listed in Table V, where each relative atomic concentration for S-1 — S-6 was calculated from data by the ASTM,[29] taking C as 100 for the major element. For the purpose of eliminating surface contaminants from the samples, preparative sparking was carried out before a

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21) A. J. Dempster, *Phys. Rev.*, **18**, 415 (1921).

22) F. A. White, T. L. Collins and F. M. Rourke, ibid., **101**, 1786 (1956).

23) F. W. Aston, "Mass Spectra and Isotopes," 2nd Ed., Edward Arnold & Co., London (1942), p. 153.

24) A. O. Nier, *Phys. Rev.*, **50**, 1041 (1936).

25) D. C. Hess, Jr., M. G. Inghram and R. J. Hayden, Plutonium Project Report, ANL-4082 (1947), p. 5.

26) W. T. Leland and A. O. Nier, *Phys. Rev.*, **73**, 1206 (1948).

27) J. Okamoto, M. Kakuta, N. Morito, Y. Nakajima, H. Tsuyama and H. Onuki, *Japan Analyst* (*Bunseki Kagaku*), **8**, 445 (1959).

28) L. Kerwin, D. E. McElcheran and M. Cottin, *Can. J. Phys.*, **35**, 783 (1957).

29) R. E. Michaelis, "Report on Standard Samples and Related Materials for Spectrochemical Analysis," American Society for Testing Materials, Philadelphia (1955), pp. 40, 46, 50.

TABLE V. RELATIVE ATOMIC CONCENTRATIONS OF THE ELEMENTS STUDIED FOR THE DETERMINATION OF THE SENSITIVITIES

The samples of copper and zinc, magnesium, and iron were prepared by the National Bureau of Standards, the Dow Chemical Company, and the Sumitomo Metal Industries, Ltd., respectively.

Element	S-1 (Cu-158)	S-2 (Zn-94b)	S-3 (Mg-66482)	S-4 (Mg-66484)	S-5 (Mg-66493)	S-6 (Mg-66851)	S-7 (Fe)
Mg		0.12	100	100	100	100	
Al	1.4	10.4	5.96	6.81	3.46		
Si	6.77		0.15	0.041			
Ca					0.102		
Cr							1.49
Mn	1.67	0.018	0.13	0.073	0.25		
Fe	1.85	0.021					100
Ni							1.36
Cu	100	1.10					
Zn	2.21	100	1.30	1.07	0.500	0.434	
Sn	0.57						

TABLE VI. CONSTANCY OF THE RELATIVE SENSITIVITY OBTAINED FROM DIFFERENT STANDARD SAMPLES

The "No." and the "Mean" indicate the number of S_X/S_R measurements and the mean weighted by the "No." for each sample, respectively.

Sample	Zn	Mg		Al		Mn	
	S_R	S_X	No.	S_X	No.	S_X	No.
S-1	1.00			1.69±0.55	23	1.28±0.35	23
S-2	1.00	2.45±0.61	21	1.66±0.81	22	1.69±0.46	12
S-3	1.00	2.06±0.13	4	1.14±0.17	3	0.66±0.04	3
S-4	1.00	1.63±0.34	7	1.23±0.34	6	1.15±0.08	4
S-5	1.00	2.75±0.10	4	1.70±0.20	3	1.18±0.17	3
S-6	1.00	2.18±0.16	5				
Mean	1.00	2.27±0.54	41	1.60±0.64	57	1.33±0.45	45

plate was first exposed. Each value of r_i used in Eq. 2 was taken from data compiled by Moeller.30)

In this work the monatomic singly-charged positive ion, the yield of which is generally larger than that of any other ion produced by a spark, such as multiply-charged or polyatomic ions, has been studied for the eleven elements shown in Table V. S_R is taken as unity for zinc, because this element is found in moderate concentrations in all the samples except for S-7 and has five isotopes, so that up to five curves can be utilized in a single calibration graph as a reference to measure the ion intensity ratio, I_X/I_R, as may be seen in Fig. 2. Strictly speaking, I_X/I_R is the "apparent" ion intensity ratio of X to R at the line density, *d*, because ions of different elements can not have the same darkening rate of a plate unless their mass ratio is very close to unity, as will be described later. Therefore, the sensitivity defined by Eq. 3 contains a factor of the darkening rate of a plate in addition to that of the ion production rate by spark discharges.

Results

Relative Sensitivity.—In Eq. 3, *S* is assumed to be independent of variations in bulk concentration. To certify this assumption, the constancy of *S* was studied using several samples. The results obtained for magnesium, aluminum and manganese are shown in Table VI and Fig. 3, where the average for each sample has been calculated by the same procedure as that used in the isotopic analyses of magnesium and zinc. The relative sensitivities obtained for the eleven elements contained in some of the samples used are shown in the second column of Table VII. For comparison with results obtained for the "sensitivity/area-factor" by several workers, the relative sensitivities divided by the square root of the corresponding mass ratio, i.e., $S_X/(m_X/m_R)^{1/2}$, are shown for some elements, taking as unity that for iron in Table VIII. Every value in the fourth column of the table was calculated

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30) T. Moeller, "Inorganic Chemistry," 4th Ed., John Wiley & Sons, Inc., New York (1955), p. 911.

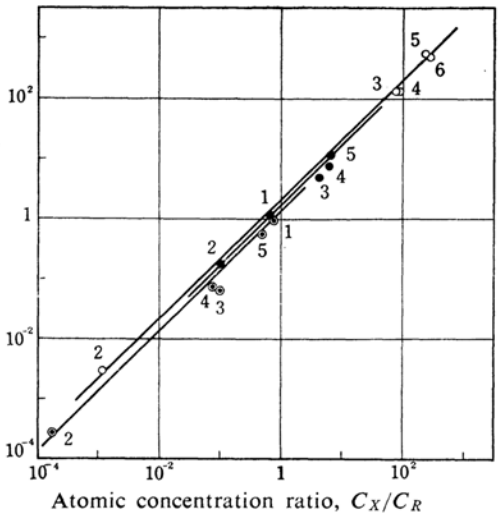

Fig. 3. Linearity of relative ion intensity versus relative atomic concentration. A figure written beside each data point indicates the number of the sample used.
○ : Mg ● : Al ◉ : Mn

TABLE VII. RELATIVE SENSITIVITIES AND RELATIVE ION PRODUCTION RATES OF ELEMENTS OBTAINED FOR MONATOMIC SINGLY-CHARGED POSITIVE IONS PRODUCED BY A DEMPSTER TYPE VACUUM SPARK ION SOURCE

Element	Relative sensitivity	Relative ion production rate	Number of measurements	Number of samples
Mg	2.3±0.5	1.4±0.3	41	5
Al	1.6±0.6	1.0±0.4	57	5
Si	1.2±0.5	0.8±0.3	31	3
Ca	2.8±0.3	2.2±0.3	3	1
Cr	2.2±1.4	2.0±1.2	17	1
Mn	1.3±0.5	1.2±0.4	45	5
Fe	1.4±0.6	1.3±0.5	37	2
Ni	1.2±0.6	1.2±0.6	8	1
Cu	0.8±0.2	0.8±0.2	24	2
Zn	1.0	1.0		
Sn	0.7±0.2	1.0±0.3	20	1

from the data for the "analysis of copper standards" shown in Ref. 34.

TABLE VIII. COMPARISON OF THE "SENSITIVITY/AREA-FACTOR" OBTAINED BY SEVERAL WORKERS TAKING UNITY FOR IRON

Element	Present work	Craig, Errock, Waldron[4]	Elliott, Craig, Errock[34]	Kai[35]
Mg	2.3±1.4	>3		14
Si	1.2±0.9	1.6	0.7	1.8
Ti		1.1		1.6
Cr	1.5±0.4	1—3	1.2	1.5
Mn	0.9±0.6	1.8	1.3	1.8
Fe	1.0	1.0	1.0	1.0
Ni	0.8±0.1	0.9	1.2	0.6
Cu	0.5±0.3	0.8		1.1
Zn	0.6±0.2	5.5	1.0	3.0
Sn	0.3±0.2	>3	2.8	
Matrix element	Mg, Fe, Cu or Zn	Al	Cu	Al or Cu

TABLE IX. RELATIVE ION PRODUCTION RATES OBTAINED WITH PHOTOMETRY AND COMPARISON WITH VALUES WITH ELECTROMETRY

	Photometry	Electrometry	
Element	Present work	Chakravarty, Venkatasubramanian, Duckworth[36]	Gorman, Jones, Hipple[13]
Mg	1.0±0.6	2.4	
Al	0.8±0.5	0.9	
Cr	1.4±0.4	1.4	1.50
Mn	0.9±0.6	2.1	
Fe	1.0	1.0	1.00
Ni	0.9±0.1	0.8	0.89
Cu	0.6±0.4	1.0	
Zn	0.7±0.3	1.9	
Matrix element	Mg, Fe, Cu or Zn	Al, Fe, Ni or Cu	Fe

Relative Ion Production Rate.—According to reports by Burlefinger and Ewald,[31] Owens,[32] and Owens and Giardino,[33] the relative darkening rate is approximately proportional to the reciprocal of the square root of the mass. On the basis of their results, it may be deduced that the number of ions necessary for the line density to achieve a certain value, d, is proportional to the square root of the mass.* Thus, applying this correction to Eq. 2, the relative ion production rate, P_X, can be obtained from the following equation:

$$P_X = P_R(S_X/S_R)(m_X/m_R)^{1/2} \qquad (4)$$

As is shown in the third column of Table VII, the range of the relative ion production rates obtained is narrower than that of the relative sensitivities. In Table IX the present

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[31] E. Burlefinger and H. Ewald, *Z. Naturforsch.*, **16a**, 430 (1961).

[32] E. B. Owens, *Appl. Spectr.*, **16**, 148 (1962).

[33] E. B. Owens and N. A. Giardino, a preprint entitled "Quantitative Mass Spectrography of Solids."

* In order to accertain this rule by isotopic analysis using the equation $r_i/r_j = (q_j/q_i)(m_i/m_j)$ instead of Eq. 1, it is necessary to choose those isotopes which are moderate in both mass ratio and abundance ratio. Perhaps ^{6}Li and ^{7}Li are the most suitable isotopes for this purpose. However, the difference in the darkening rate between them is calculated to be no more than 8 per cent. Therefore, the difference in the mass effect among the isotopes of an element of a larger atomic number, such as copper, is negligibly small compared with the erratic fluctuations in the photometry. This is the reason why no correction for the darkening rate is made for any of the isotopes in Eqs. 1 and 2.

data are compared with values determined by the electrometry, taking P_R as unity for iron.

The Constancy of the Relative Ion Yields for Elements.—As may be seen in Fig. 2, the data points for every ion do not exactly fall on a smooth curve. This is presumably due to fluctuations in the relative ion yields for different elements in each exposure, to the non-uniformity of the emulsion of the photographic plate and, to errors in the measurements of both the monitor current and the photometry of the plate. From this point of view, the reproducibility of the relative ion intensities measured for various ions has been studied in every exposure stage using a modified Mattauch-Ewald method. This method employs D_n and $\log r$ as the two components of a calibration graph, while Mattauch-Ewald's method employs $(L_0-L)/L_0$ and r. The former has such advantages over the latter as follows:

(1) A calibration curve with a linear part is always obtainable for the isotopic ions to be used as internal standards only if the most suitable expression of density among the five is employed.

(2) Extrapolation is applicable to the curve according to each "useful range" shown in Table I.

TABLE X. REPRODUCIBILITY OF RELATIVE ION INTENSITIES MEASURED FOR ISOTOPES AND DIFFERENT ELEMENTS USING THE SAMPLE S-1

Ions	Ion intensity ratio	Number of measurements	Precision %
$^{56}Fe^+/^{54}Fe^+$	14.9±1.4[*1]	22	± 9
$^{120}Sn^+/^{118}Sn^+$	1.38±0.13[*2]	20	± 9
$^{66}Zn^{2+}/^{68}Zn^{2+}$	1.55±0.13[*3]	26	± 8
$^{120}Sn^{2+}/^{118}Sn^{2+}$	1.41±0.12[*2]	24	± 9
$^{27}Al^+/Zn^+$	0.913±0.357	38	±39
$^{55}Mn^+/Zn^+$	0.882±0.524	43	±59
$^{56}Fe^+/Zn^+$	1.02±0.52	42	±51
$^{120}Sn^+/Zn^+$	0.0577±0.0180	29	±31
$^{27}Al^+/^{56}Fe^+$	1.03±0.49	38	±48
$^{55}Mn^+/^{56}Fe^+$	0.980±0.260	42	±27
$^{120}Sn^+/^{56}Fe^+$	0.0829±0.0445	17	±54
$^{27}Al^+/^{120}Sn^+$	13.7±7.1	14	±52
$^{55}Mn^+/^{120}Sn^+$	14.6±5.7	17	±39
$^{27}Al^+/^{55}Mn^+$	1.01±0.30	38	±30
$^{27}Al^{2+}/^{66}Zn^{2+}$	1.91±1.02	10	±53
$^{55}Mn^{2+}/^{66}Zn^{2+}$	2.92±1.46	29	±50
$^{120}Sn^{2+}/^{66}Zn^{2+}$	0.402±0.247	16	±61
$^{55}Mn^{2+}/^{120}Sn^{2+}$	10.3±5.4	13	±52
$^{27}Al^{2+}/^{55}Mn^{2+}$	0.583±0.186	13	±32
$^{27}Al^{2+}/Zn^+$	0.167±0.098	18	±59
$^{55}Mn^{2+}/Zn^+$	0.257±0.097	37	±38
$^{66}Zn^{2+}/Zn^+$	0.110±0.059	33	±54
$^{120}Sn^{2+}/Zn^+$	0.0330±0.0115	28	±35
$^{27}Al^{2+}/^{27}Al^+$	0.138±0.047	14	±34
$^{55}Mn^{2+}/^{55}Mn^+$	0.334±0.124	35	±37
$^{120}Sn^{2+}/^{120}Sn^+$	0.613±0.144	23	±23

[*1–*3] These are in good agreement with values determined by electrometry as shown below:

Fe: 15.77±0.03 (Ref. 18)
Sn: 1.377±0.007 (Ref. 18)
Zn: 1.501 or 1.505 (Ref. 15)

For the purpose of determining the relative intensities of ions detected in the "same" exposure stage, the present method is more suitable than the monitor method, because all the r_i, r_j,…… values in the abscissa are free from erratic fluctuations.

The results are shown in Table X, where the singly-charged ions of the isotopes of zinc contained as one of the impurity elements in S-1 are employed as the internal standards for calibration, and no value in the second column is corrected for the darkening rate.

Discussion

It will be found in Table X that the results obtained from repeated measurements of many pairs of different elements are less reproducible by several times than those for isotopes. It is the same with those of four pairs of the same element with single and double charges. The results may suggest that the spark source does not always possess a constant ionization efficiency for all the elements contained in the sample electrodes and/or the relative ion transmission rates from the source to a plate are not always constant for all the ion species produced, probably due to the fluctuations of spark conditions during the exposures, rather than the sample used is not mass-spectroscopically homogeneous in chemical composition. It is possible, with a spark ion source, that on spark spots the chemical composition of the sample electrodes, even if they are originally homogeneous, may be varied during spark discharges because of fractional evaporation, selective sputtering, preferential diffusion, etc. The precision for each pair of iron, zinc and tin isotopes shown in Table X can be considered approximately to indicate the errors attributed to the non-uniformity of photographic emulsion and development in the present work.

Although it may be necessary to study further the elements using many samples different in concentration, Fig. 3 is believed to establish that the relative sensitivity of each element is constant, independent of changes in the bulk concentration of the element to within an uncertainty factor of 1.5 on the average; this compares favorably with the results obtained by Hannay and Ahearn using several samples of both silicon and germanium, including boron and antimony as impurity elements respectively.[11] Table VII indicates that the relative sensitivities are of the same order of magnitude for all the elements studied in spite of large differences in physical and chemical properties among them, and it is also so with the relative ion production rates. This approximate equality is generally accepted for the Dempster-type vacuum-spark ion source.[3, 4, 34, 36–38]

Owens and Giardino discovered that the relative sensitivity of gallium with respect to arsenic increased considerably in value after prolonged sparking.[33] This discrimination effect was also observed with magnesium and zinc by Duckworth et al.[36] using several alloys, and accepted with zinc by Waldron, who has stated (cf. Ref. 36) that the sensitivity ratio of zinc to iron was found to get much lower values than 5.5 (cf. Table VIII) in subsequent measurements. In the present work, ions produced during the early stage of sparking were studied. As Table VIII shows, the values obtained by the four groups of workers have a large discrepancy among them for magnesium, zinc and tin, although they do not differ for the other elements by more than a factor of 2. This is possibly due to either the above discrimination effect in sparking, to matrix effects, or to both; Craig has found that the relative sensitivity of zinc with respect to iron is about 1 for some matrices, e. g., copper and gallium, but about 6 for other matrices, e. g., aluminum and iron.[39] It may be seen from Table IX that the ion production rates for each element agree also to within a factor of 2 among the three works in spite of the essential differences in detection methods.

On the basis of these considerations, it might be concluded that:

(1) The relative ion yields from a spark source are not always constant for all the elements contained in the sample electrodes even if the operating conditions of the instrument are kept constant throughout the exposures.

(2) This can cause variations in the relative sensitivities by up to several tens of per cent.

(3) Under different experimental conditions, the relative sensitivities are apt to change remarkably for some elements, such as magnesium, zinc and tin although they seem to change rather slightly for others, such as chromium, manganese and nickel.

(4) Since they are subject to changes of value according as various conditions, perhaps they can not be generally applicable as the analytical constant without uncertainty factors, such as about 2 for non-volatile elements and more for volatile ones.

However, much more work must be done to obtain precise informations on the sensitivity.

Summary

The relative sensitivities of eleven elements in a spark-source mass spectrograph have been determined for monatomic singly-charged positive ions detected with Ilford Q2 plates. The results show that the elements have approximately the same sensitivities to within a factor of 3 in spite of large differences in both physical and chemical properties among them, and that the sensitivity of each element is constant in value within an uncertainty factor of 1.5, independent of changes in the bulk concentration of the element. Relative ion production rates have also been determined from the above sensitivities; they are in reasonable agreement with published values determined by electrical detection. From repeated measurements of the relative intensities of various ions, it has been suggested that relative ion yields from a spark ion source are not always constant for different elements. On the basis of these investigations, a discussion has been made of the general applicability of the sensitivity as the analytical constant in the quantitative mass spectrography of solids. Five different formulas have been used to express the "density" of mass lines, and exposures have been determined with an integrated monitor current. By trying several isotopic analyses, the calibration methods have been shown to be useful for mass spectrography.

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34) R. M. Elliott, R. D. Craig and G. A. Errock, "Instruments and Measurements," Vol. I, Ed. by H. Koch and G. Ljungberg, Academic Press, New York (1961), p. 271.

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36) B. Chakravarty, V. S. Venkatasubramanian and H. E. Duckworth, "Advances in Mass Spectrometry," Vol. II, Ed. by R. M. Elliott, Pergamon Press, London (1963), p. 128.

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38) R. Brown, R. D. Craig and R. M. Elliott, "Advances in Mass Spectrometry," Vol. II, Ed. by R. M. Elliott, Pergamon Press, London (1962), p. 141.

39) R. D. Craig, private communication.

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