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A Critical Study of the Primary x-Ray Method of Chemical Analysis

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Introduction

A large number of independent variables peculiar to the method and apparatus come into play when x-ray spectrography is used for the purpose of chemical analysis. It is necessary that these variables be evaluated from the standpoint of the chemist so as to enable him to carry out his work of analysis with a greater degree of accuracy and dispatch, and to allow a reliable duplication of results.

The spectrograph and accessories used in connection with this investigation were the newer type of Siegbahn apparatus, especially adapted to chemical work.[2] The spectrograph is flattened on the tube side and has a radius of 12.7 cm. An excellent specimen of calcite was used throughout for the diffracting crystal.

Constant, fully rectified voltage with a minimum of ripple was supplied from a power plant consisting of suitably constructed and connected Kenetrons, transformers, inductance, condensers and voltage regulator.

Experimental

The sample was prepared by hammering the powder into the surface of a pitted copper anticathode wedge. The filament employed was the BaO–SrO on platinum wire of 0.017 inch diameter, wound in a flat spiral of definite dimensions.

Control of Uniformity of Emission of Electrons from Filament.—If there are any irregularities in the filament either as regards winding or oxide coat, an uneven distribution of electrons is obtained on the focal spot, which will show to a lesser degree on the plate. The rocking of the crystal minimizes the effect to some extent but the amount of variation might be large enough in certain cases to cause serious difficulty in making reliable quantitative measurements.

This difficulty was practically obviated in this work by means of the following procedure. The filament winding was made regular, smooth, and tight and carefully centered in the electron shield, so that on heating no comparatively dark or light spots occurred. The face of the anticathode was then turned toward the peep-window in the tube, the apparatus evacuated, the x-ray power turned on and the focal spot examined with a telescope. Wherever an electron strikes the anticathode, pronounced fluorescence takes place, so that the visual determination of the evenness of distribution of the electron stream over the focal spot is a simple one. All exposures in a given series were made with such a filament without recoating or change of position. Thus any discrepancies in one exposure of a group is repeated in all of them without affecting their relationship to one another, as far as the filament is concerned.

The best and least time consuming method for regulation of the electron stream would be to rotate the filament

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(1) J. T. Baker Chemical Company Fellow in Analytical Chemistry for 1932–33. Eastern Division. Extracts from a thesis presented to the Faculty of the Graduate School of Cornell University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) M. Siegbahn, "Spectroscopy of X-Rays," Oxford University Press, London, 1925; M. Siegbahn, "Röntgenspektroskopie," J. Springer, Berlin, 1931; A. Lindh, "Röntgenspektroskopie," (Handbuch der Experimental Physik), Akademische Verlagsgesellschaft m. b. H., Leipzig, 1930, Vol. 24; A. Schliede and E. Schneider, "Röntgenspektroskopie und Kristallstrukturanalyse," Walter de Gruyter and Co., Leipzig, 1929; G. von Hevesy, "Chemical Analysis by x-Rays and its Applications," McGraw-Hill Book Co., New York, 1932; Eddy, Laby and Turner, *Proc. Roy. Soc.* (London), **124**, 249 (1929); Eddy and Laby, *ibid.*, **127**, 20 (1930); Laby, *Trans. Faraday Soc.*, **26**, 497 (1930); Gunther and Stranski, *Z. physik. Chem.*, **118**, 257 (1925).

continuously through an angle of 180° in some such manner as the crystal is rocked. Thus all parts of the focal spot will cover all the active portions of the crystal, and any irregularities, due to the filament, will be smoothed out as far as the plate is concerned.

The mechanics of exposure control, such as maintenance of x-ray power, method of counting time of exposure, photometry, type of plate, general plate treatment, etc., were kept constant throughout the course of the work.

Sensitometrically, duplicate exposures were considered satisfactory if the values obtained from the plates agreed to within 5%, while duplicate photometric measurements of the same line were repeated until agreement to within 1% was obtained. The peak method of measurement was used; this procedure is suitable only when lines of a K series are compared with other lines of a K series, and lines of an L series with other lines of an L series, etc.

Variables of the Spectrograph in Operation

In order to arrive at some basis for producing duplicable results, each adjustable portion of the spectrograph was varied systematically to determine what effect, if any, such a change would have on the intensity of the line recorded on the photographic plate. For each one of the variables determined, all other variables were fixed for the duration of the experiment as completely as possible, either at some arbitrary or predetermined value.

Sufficient data have been collected by numerous investigators[3] to clear up the nature of variation of intensity with voltage and the effect to be expected should two elements of decidedly different excitation potentials be examined in the same exposure. For the present work, for critical voltages up to 17.5 kv., twice the critical voltage was used if the lines of a single element were considered, while, if two or more elements are present, twice the value necessary for the highest atomic element on the anticathode was used.

Varying the current through the tube from 4–18 m. a., and using the Cu K lines and the Ag L lines as bases of measurement, it was found that the plate factors, intensity, opacity and density were proportional to the milliamperage, that of opacity only being a straight lined function. An investigation of variation of intensity with m. a., and at the same time varying the voltage, has been carried out by Nasledow and Scharawsky.[4]

Next, the time of exposure was varied through the analytical range in one minute intervals, the first and second order Cu K lines, and the Ag L lines being used as bases of measurement. Again, all the plate factors were found to be proportional to the time of exposure, that of opacity only being a straight lined function.

Varying the tilt of the anticathode from 0–40° from the position normal to the plane of emission of electrons, it was again found that the plate factors increased with increase in amount of tilt even beyond the limit (40°) listed, that of opacity only being a straight lined function. The L lines of Pd, La, Ag, Pt and Ba were used as bases of measurement.

For the variation of rocking angle the Pd, Ag, La, Pt L lines and the Ge K lines were used as bases of measurement. The experiments showed that for quantitative work a rocking angle of 60 minutes or less should be used to maintain a region of constancy on the plate, while for qualitative work a much wider angle, up to three or four degrees may be used to advantage.

The effective area of the plate was determined for the Cu K lines and the Ag L lines by continually shifting the zero point of the crystal away from its correct focus in small intervals. The region of constant line intensity was again found to be 60 minutes for both elements investigated while the total plate area affected was considerably larger for the long wave lengths than for the short. Thus, if two lines of the same exposure are to be compared with each other, they should be equidistant from the center of focus of the crystal and separated by not more than 1.0 degree of wave length.

Varying the size of the focal spot by changing the relative position of the electron shield showed that the three plate factors are approximately inversely proportional to the diameter of the focal spot. The Cu K lines and the Ag L lines were used in this series of measurements.

Other variables, such as slit-width, variations in intensity with change in atomic number of metal used as anticathode wedge, screen material between tube and spectrograph, filament material, variation in reflecting power per unit surface of crystal, etc., pertain to problems of a special nature and were not evaluated here, beyond maintenance of their constancy.

Conclusively, the results of the foregoing experiments emphasize the fact that, for consistent and duplicable results, a standard mechanical procedure be rigidly adhered to, so that for all purposes all the variables of the apparatus will function as a single definite constant. In other words, only comparative analyses made under exactly analogous conditions may lay any claim to exactness.

Exposure and the Photographic Emulsion

Strictly speaking, the "plate characteristic" as originally evaluated by Hurter and Driffield consists of the logarithm of radiation intensity against the density obtained from the plate. For light in the optical range, a curve of three portions is obtained, representing under-, correct- and over-exposures, the correct exposure being a straight lined function. On comparison of x-ray exposures with ordinary light exposures, it will be seen that the curve for x-rays corresponds to the under-exposure region for a plate used in the frequency range of visible light (see Fig. 1). Consequently, the original definition of plate characteristic has little meaning when applied to x-ray images.

Now, for light-exposed plates, a correct exposure is indicated when the density is directly proportional to the logarithm of the time of exposure. A graph of this function for the x-ray plate used here[5] shows that most of the densities lie on a straight, or nearly so, line, with an upward

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(3) See reference 2 above and also Webster and Clark, *Phys. Rev.*, **9**, 571 (1917); Wooten, *Phys. Rev.*, **13**, 71 (1919); Kettmann, *Z. Physik*, **18**, 359 (1923); Stumper, *ibid.*, **36**, 1 (1926); Jannson, *ibid.*, **36**, 426 (1926); Allison, *Phys. Rev.*, **30**, 245 (1927); and *Phys. Rev.*, **32**, 1 (1928); Nasledow and Scharawsky, *Physik. Z.*, **28**, 549, 625 (1927); Lorentz, *Z. Physik*, **51**, 71 (1928).

(4) Nasledow and Scharawsky, *Z. Physik*, **41**, 2–3, 155 (1927); and **42**, 11, 870 (1927).

(5) The plates used were the "Eclipse Ortho Soft, Speed 650," manufactured by the Imperial Dry Plate Co., Ltd., London, having a large grain size and a thin coating of emulsion.

flexion for the extremely long exposures (see Fig. 2). In other words, the density is proportional to log time for a properly exposed x-ray plate, the idea of under-exposure having little meaning. This suggests that a much better classification of photographic emulsions for x-rays would be obtained by use of the density–log time relation than the usual density–log intensity graph.

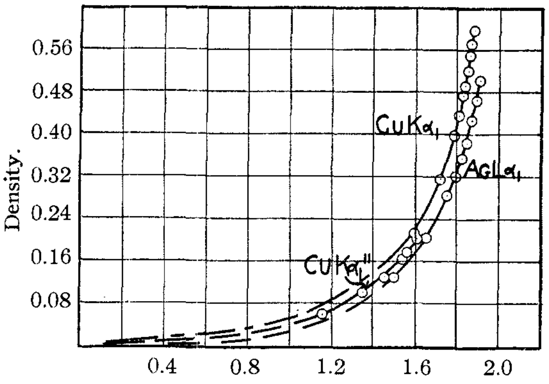

Fig. 1.—Variation of density with log intensity.

Since density is $\log_{10}$-opacity, an explanation for the straight lined variation of opacity with so many of the variables, discussed previously, is suggested.

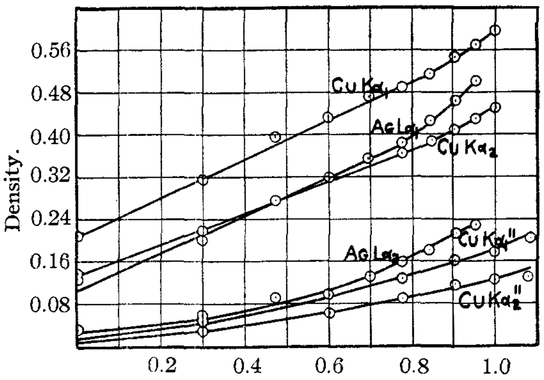

Fig. 2.—Variation of density with log time.

Plate Sensitivity

A curve covering the short wave length region up to 1.7 Å. showing the "sensitivity" of the plate to x-rays of varying wave length has been given by Hevesy.[6] An expansion of the range of wave lengths for the chemically usable x-ray region was thought advisable.

Several elements, either as such or in the form of compounds, representing the wave length range 1000–4500 X. U., were exposed on the same plate under the same conditions of current, time, etc., the voltage being varied to suit the particular substance on the anticathode. The plate densities obtained with the compounds were converted to the values the respective elements would have if they were not diluted, by multiplying the plate values by the usual chemical factors. Checking three of these results by experiment showed that no serious error is introduced by this procedure (see Figs. 3 and 4).

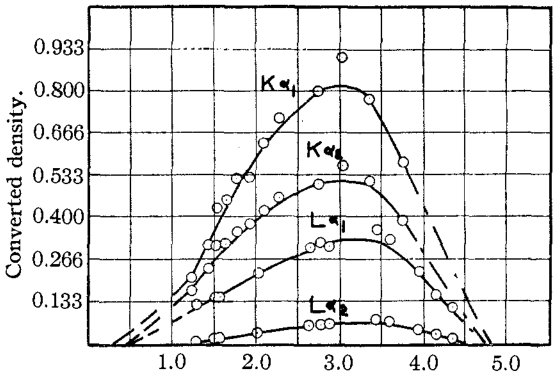

Fig. 3.—Variation of converted densities with wave length.

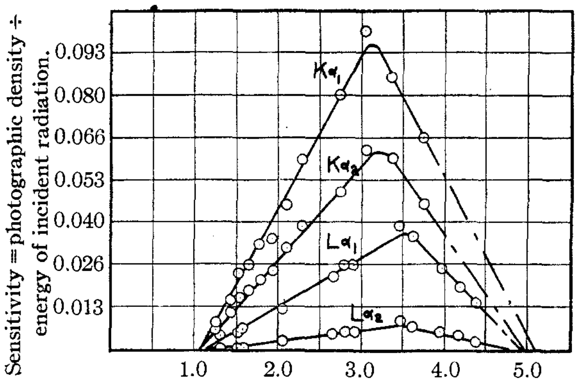

Fig. 4.—Wave length sensitivity, densities converted directly.

Since the peak method of measuring intensities was used, the K and L series do not fall on the same curve. Much of the difference is eliminated when the area between the two branches of the intensity curve is taken as a measure of intensity.

The peaks of the various curves lie in the region of 2800–3600 X. U. This is to be expected since the L absorption for Ag also occurs here.

Time Factor Curve

In order to determine the time of exposure necessary to obtain approximate equality of density for widely divergent wave lengths, the following type curve was constructed. The density values from the wave length–density curve were divided into the peak value for the individual curve, and the factors obtained graphed against wave length (see Fig. 5). These curves give, on proper calibration, the factor to be used in multiplying the time of exposure at the peak wave length in order to obtain the time of exposure necessary for any other wave length in the range examined. Experimental checking of the curve showed it to be a useful approximation.

Experiments showed that such a curve may be applied to any given percentage, by determining the time neces-

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(6) See (2) above, page 63.

sary to reach a given density with one element, and applying the result to the curve. The results are expected to be valid only when the same diluent is used in each case.

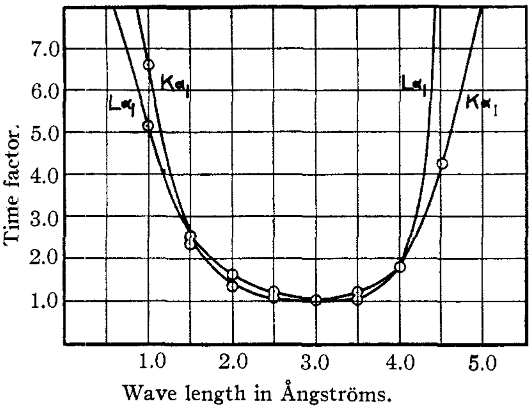

Fig. 5.—Variation of exposure factor with wave length, converted densities.

Concentration Relations

The two general methods of quantitative analysis by x-ray spectroscopy, employing primary excitation procedures, are those developed by G. von Hevesy and T. H. Laby.[2]

The Hevesy method of admixture of a reference substance is cumbersome in that it requires an excessive number of exposures per sample of a single percentage while the Laby method is restricted to elements of neighboring atomic number.

An absolute method of analysis should be possible providing the variables discussed previously have been defined properly at some fixed point. The lines of a single element only would be considered, the percentage being read directly from the density on the plate. Empirical mixtures of the material, which are close replicas of the original, are made up with the element to be examined varying in known amounts; all exposures are placed on the same plate; the determined plate values are then suitably graphed. The analysis of an unknown of similar elementary composition similar to the standard mixtures, consists in placing properly exposed lines on the curve and reading off the percentages from the graph. In general, this is the relative method of spectroscopic estimation as used in the optical range. Its success depends on at least two factors: (1) the definition and fixation of the variables previously defined so that under selected conditions the same results are always obtained. Experiments conducted along this line have shown that such a goal is possible, at least within the limits of accuracy of any chemical spectroscopic analysis, providing the same filament coating is used. (2) One other vital factor which is not mentioned by either Laby or Hevesy is that of uniformity of emission of electrons per unit area over the surface of the filament under working conditions, that is, when the filament has to be recoated from time to time. If such strict uniformity is not found to exist, the method as outlined above is inapplicable since a displacement along the density axis will result which will not be due to a change in concentration. Obviously, the discrepancies due to excitation and absorption effects of other elements will be ruled out in the method suggested because of the similarity of standards and unknowns.

Two elements, iron and calcium as oxides, were mixed with oxides of other elements (Table I). Each plate contained one complete percentage series, as Fe–Be, Fe–Ca, etc. A fresh filament was prepared for each set of samples by suitably applying barium and strontium compounds to a platinum wire. The purpose of the change of the filament coating after each series was to determine the constancy of emission of electrons from the filament under ordinary conditions of analysis, where frequent changes of filament are necessary.

The time of exposure was selected from the time factor curve. All precautions, conditions, details of exposure, proper variation of apparatus, etc., were defined at the values best suited to the analysis in hand by means of the experiments previously described. These conditions were rigidly adhered to throughout in order that the results may be considered comparable.

TABLE I

PLATE DENSITY VALUES FOR $K\alpha_1$ LINE FROM PREPARED SAMPLES

Fe, %	10	20	30	40	50	60	70
$Fe_2O_3 + BeO$	0.13	0.18	0.22	0.27	0.33	0.36	0.42
$Fe_2O_3 + Al_2O_3$	.07	.14	.20	.24	.29	.33	.38
$Fe_2O_3 + CaO$	.06	.12	.18	.23	.28	.30	.34
$Fe_2O_3 + Cr_2O_3$	.07	.16	.22	.26	.30	.32	.34
$Fe_2O_3 + NiO$	.22	.26	.29	.32	.35	.38	.41
$Fe_2O_3 + SrO$	.30	.33	.36	.39	.42	.45	.47
$Fe_2O_3 + SnO_2$	.35	.40	.43	.45	.47	.49	.51
$Fe_2O_3 + UO_2$	.11	.18	.24	.29	.32	.36	.38
Ca, %	10	20	30	40	50	60	71.5
$CaO + BeO$	0.20	0.29	0.36	0.43	0.48	0.53	0.55
$CaO + Al_2O_3$	.19	.27	.33	.39	.44	.49	.53
$CaO + Fe_2O_3$	.29	.35	.39	.42	.45	.47	.49
$CaO + ZrO_2$	.26	.32	.36	.39	.41	.43	.44
$CaO + SnO_2$	.33	.38	.41	.44	.47	.49	.51
$CaO + UO_2$	.20	.33	.42	.45	.48	.50	.52

Analytical Results

The last column in the numerical table lists the plate values for pure Fe_2O_3 and pure CaO. These show that the oxide filaments as ordinarily prepared in the laboratory do not give the same emission per unit surface from coat to coat, doubtless due to variation in thickness. In other words, the usual oxide coat is unsuitable for the purpose of the relative method of estimation as outlined above.

However, smooth and regular concentration curves (Figs. 6 and 7) can be obtained as long as the same filament coating is used. This suggests that the relative method will be a suitable one for quantitative estimation by means of cathode ray excitation of x-rays as soon as a filament is found which will give a sufficiently uniform emission of electrons regardless of usage, so that the final values of each curve as listed here would be coincident with each other.

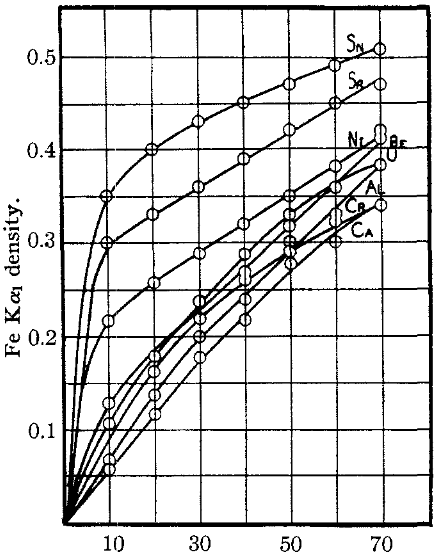

Fig. 6.—Density-percentage iron variation of plate density of iron as oxide mixed with oxides of elements indicated.

Finally, the presence of other elements markedly alters the shape of the curve in a manner somewhat dependent on the atomic number of the added element, qualitatively agreeing with the results of Coster and Nishina.[7] Several of the curves are approximately parallel from about 10 or 20% up to 70% of the metal examined; for these mixtures the Laby method would be applicable provided the proper filament coating is used.

The variation in atomic number is evident from the fact that the curves of the added elements of much higher atomic number than that of the element examined have approximately the same shape, while curves of much lower atomic number are also similar to each other.

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The writer wishes to extend his thanks to Professor Jacob Papish of Cornell University for affording the facilities for carrying on the experimental work and for suggesting the subject matter of the paper.

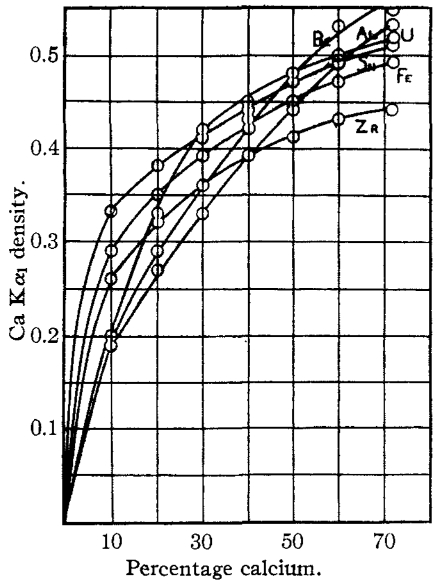

Fig. 7.—Density-percentage calcium variation of plate density of calcium as oxide mixed with oxides of elements indicated.

Summary

1. It is shown that a definitive standardization of the variables of the spectrograph, photographic plate, analytical procedures, etc., must be adhered to rigidly in order to obtain comparable results of analytical worth.

2. The use of log time-density was found to be a more suitable function for defining the plate characteristic for x-ray exposures than the usual log intensity-density.

3. An absolute method of x-ray spectroscopic estimation from predetermined curves will be suitable for analysis provided a filament which gives a uniform emission of electrons be used.

ITHACA, N. Y. RECEIVED JANUARY 30, 1934

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(7) Coster and Nishina, *Chem. News*, **130**, 150 (1925).