# The Measurement of Electron-Diffraction Intensity by a Digital Voltmeter

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Nearly all measurements in physical chemistry are currently based on the conversion of the quantities to be measured into electric current or voltage, which is usually recorded on a sheet of chart paper by an automatic pen-recorder. As a result of recent advances in electronics, however, it is now possible to make measurements in a digital form by means of an analogue-to-digital converter, which has the following advantages: a) In comparison with analogue measurements, errors from various electric sources (random noises generated in amplification, transmission, *etc.*) and mechanical sources (friction in pen recording, uncertainties in the chart scale, *etc.*) can be decreased or eliminated.

b) The measurements can not only be made more easily and rapidly, but also the outputs can be used more directly as input data to an electronic computer for a subsequent data analysis.

c) The measurements can be made much more precisely, since the readings can be integrated for an arbitrary length of time, or the results of several repeated scannings can be superimposed. This procedure improves the signal-to-noise ratio appreciably.

The present note will report on the application of the above technique to the microdensitometry of electron-diffraction photographs.[1]

## Procedure

The scattered electron intensities recorded on a photographic plate were measured by a microphotometer (Rigaku Denki MP3),[2] as is shown in Fig. 1. The electric current from a photomultiplier (RCA 931A), about 0.1 $\mu$A, was grounded through a high-precision resistor of 10 M$\Omega$ installed in an integrating digital voltmeter (Takeda Riken TR-65A15, 10 kc per volt); hence, no pre-amplifier was necessary. The output voltage, read out in five significant decimal digits, was recorded by a digital printer (TR-6191). The basic conditions for the measurement were adjusted in the following way. The detector system was found to have sufficient precision and stability for carrying out the required tests.

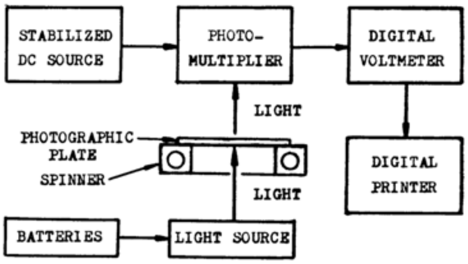

Fig. 1. The digital densitometry of a photographic plate.

*a) Dark Current.* When no incident light was present and the d. c. voltage of 320 V, was applied to the photomultiplier, the photocurrent was about $1.5\times10^{-9}$ A, and no appreciable irregular fluctuation was observed during the measurement.

*b) Optical System.* It was possible to obtain an optical source of sufficient stability and linearity by supplying a lamp with a d. c. current of about 2.5 A from a pair of two 6-V batteries (108 A hr) connected in parallel. The brightness of the light decreased with time in the ratio of about $3\times10^{-5}$ per minute.

*c) Photoelectric Stability.* The random noises in the photocurrent with periods of more than a few tenths of a cycle per second can be rejected by an integrating measurement with a gate time of a few seconds. The photomultiplier was used with a lowered sensitivity with a d. c. voltage of about 320 V across Electrodes 9 and 11 of the 931A tube. Care was taken to stabilize this d. c.

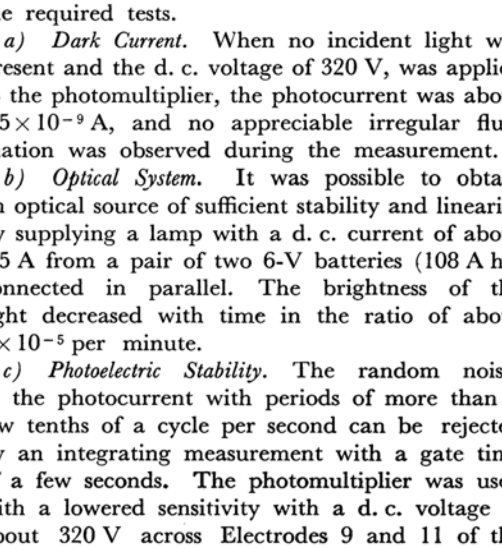

Fig. 2. Typical variations in the photocurrent corresponding to the light incident through a point of constant density on a photographic plate.

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[1] L. S. Bartell and H. K. Higginbotham, *J. Chem. Phys.*, **42**, 851 (1965); L. S. Bartell and B. L. Carroll, *ibid.*, **42**, 1135 (1965); D. A. Kohl, Thesis, Indiana University (1966).

[2] Y. Morino and T. Iijima, This Bulletin, **35**, 1661 (1962); Y. Morino, K. Kuchitsu and Y. Murata, *Acta Cryst.*, **18**, 549 (1965).

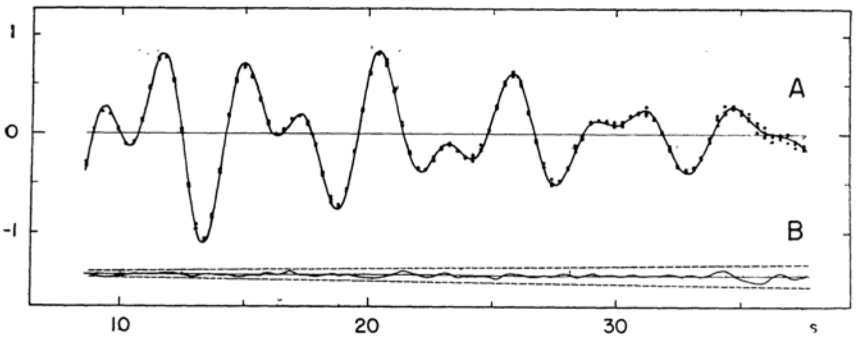

Fig. 3. The molecular intensity for $BF_3$. (A) The observed values from three photographic plates are shown in dots. Mutual discrepancies indicate the order of magnitude of the errors in the present digital measurements. The solid curve corresponds to the theoretical intensity for the most probable structure model. (B) A typical residual (obs. minus calc.). The broken curve represents the error in the molecular intensity due to the relative error of $1\times10^{-3}$ in the original photocurrent.

voltage, since the fluctuation in this voltage, $\Delta V$, was found to cause the photocurrent, $i$, to fluctuate with the rate of $\Delta i/i\approx7\times\Delta V/V$. A slight fatigue in the photoelectric surface (a nearly uniform decrease in the photocurrent response to a constant incident light) and a slight after-effect (an increase or decrease in the photocurrent for several seconds immediately after a big change in the incident light) were detected. As is shown in Fig. 2, the photocurrent was found to decrease at the rate of about $1\times10^{-4}$ min when the multiplier was exposed to a constant incident light, with random deviations from linearity of about $1.5\times10^{-4}$.

*d) Mechanical Operations.* The reproducibility of the precision screw which travels the photographic plate was about 0.01 mm; it was found to be sufficiently systematic. Hence, the error from this source was eliminated by making the measurements across the full diameter of the spinning plate and by taking the average of the measurements on both sides.[1] In an ordinary operation, several succesive measurements at a gate time of 4 seconds were averaged for each point on the photographic plate taken at regular intervals of about 0.3 mm.

*e) Accuracy.* The relative random error in the measurement of the photocurrent was found to be about $2\times10^{-4}$ on the average; usually it was less than $5\times10^{-4}$. A photographic plate with a density of from 0.3 to 0.6 causes a random error of roughly 0.02 in the reduced molecular scattering intensity, $sM(s)$. The systematic error due to the flaws in the photographic plate can, of course, be eliminated by examining the measurements made on several different plates.

TABLE 1. A COMPARISON OF THE CHART AND DIGITAL MEASUREMENTS

| | Time required | Precision | Accuracy[a] |
|---|---|---|---|
| Chart measurement | *ca.* 9 hr | $2\times10^{-4}$ | *ca.* $6\times10^{-4}$ |
| Digital measurement | *ca.* 2 hr | $2\times10^{-5}$ | *ca.* $3\times10^{-4}$ |

[a] General judgement on the reliability of the measurements.

**Comparison with Chart Measurements.** As is shown in Table 1, the present digital procedure has resulted in an appreciable decrease in the time and labor and in a tenfold increase in the precision of the measurement. In the present stage, it seems that the digital measurement is roughly twice as accurate as the previous chart measurement.[2] The present accuracy does not seem to be very distant from the ultimate accuracy of the photographic detection of electron-scattering intensities.

**Application.** The present method has been applied to the study of boron trifluoride by gas electron diffraction.[3] The random fluctuations in the readings of electron intensities were within the range of the above estimates (*e*). From the molecular intensity shown in Fig. 3, the B–F bond distance was determined with a random error of 0.0005 Å and a total uncertainty of about 0.001 Å.

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[3] K. Kuchitsu and S. Konaka, *J. Chem. Phys.*, **45**, 4342 (1966).