

ENGINEERING RESEARCH INSTITUTE
UNIVERSITY OF MICHIGAN
ANN ARBOR

FINAL REPORT

EXCITATION AND DIRECT-READING METHODS
FOR SPECTROCHEMICAL ANALYSIS



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Project M567

LEEDS AND NORTHROP CO.
PHILADELPHIA, PA.

July, 1954

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A STUDY OF EQUIPMENT FOR QUANTITATIVE
SPECTROCHEMICAL ANALYSIS

INTRODUCTION

This, the final project report is divided into two parts. Part A is a short review of the work that has been reported in nine M567 progress reports and an unpublished paper presented at the annual meeting of the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. The subject and date of each report or paper is stated in the table of contents of this report. Closely related to this material is an M866 progress report, dated July 7, 1950. The sponsor of this project was the Western Cartridge Company of East Alton, Illinois. The report deals in part with the Leeds and Northrup source installation at that company.

Part B is a general summary of the early work on sources and the U. of M. photoelectric equipment, followed by a discussion of the work with the spectrochemical analyzer and the unpublished Pittsburgh paper of March 5, 1954.

A. REVIEW OF PROJECT WORK REPORTED IN
PRECEDING PROGRESS REPORTS AND PAPERS

1. A Study of the Synchronous and Air-Gap Spectrographic Spark Sources,
July 3, 1945

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Discussion. The contents of this report deal only with the spark-source circuit and its electrical operation. Some of the important results of this period were: (1) building the source, (2) an air-interrupter design giving a stable breakdown voltage, (3) the synchronous interrupter was not shown to be superfluous, (4) direct coupling of an oscilloscope to the high-voltage-condenser section, (5) establishing a notion of the circuit operation, electrical properties of an air gap, power requirements, and essential meters.

2. A Study of the Controlled Spectrographic Spark Source, October 10, 1946

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Discussion. A paper on this study of sources was given at the ASTM meeting, held in Buffalo, N. Y. in June, 1946. The paper was published in the ASTM Special Publication No. 76, 1948. The important points for this period were: (1) small changes in air-interrupter design and a change from tungsten to magnesium electrodes improved the stability of the source at low energy operations and eliminated the need for the synchronous interrupter, (2) introduction of the spark-initiated, 60-cycle, a-c arc and the application of a high-voltage rectifier tube for alternate half-cycle spark or arc source operation, (3) photomultiplier tube, two-gun oscilloscope, and ratio recorder adaptation with quartz prism spectrograph for the purpose of recording instantaneous and short-time integrated radiation, (4) photoelectric observations of optically filtered bands from the ultra violet region, the type of radiation now being utilized in the Leeds and Northrup direct reader as a reference signal, (5) data obtained with a moving-film camera of the two-gun oscillograph pattern showing the successive spark-to-spark fluctuations of such events as condenser discharge voltage, filtered radiation, and dispersed single line intensities.

3. American Steel and Wire Company Source Installation, June 24, 1947

This is a short report on the first Leeds and Northrup trial source installation. The main points from this report are as follows:

a. The 3/8-inch-diameter magnesium air-interrupter electrodes had to burn to a "normal" dome shape for optimum breakdown voltage stability.

b. Tests were run which showed that spark line intensities in steel analysis did not vary appreciably when the source parameters were changed from a high peak current (1000 amperes) and 1 or 2 sparks per half cycle to a lower peak current (500 amperes) and 4 or 5 sparks. The r.f. current was kept about the same.

c. The spark-initiated a-c arc was compared in sensitivity with a conventional high-voltage a-c arc at the University of Michigan. No difference was observed in detecting 0.005% Mo.

d. Some changes in electrical parameters and air-interrupter design were suggested. This source unit remained with the American Steel and Wire Company in Cleveland, Ohio.

4. Universal Cyclops Steel Corporation Source Installation, November 12, 1947

This short report deals with the second trial source installation. The main points are:

a. An important analysis at Universal Cyclops was 0.01 to 1.0 percent Si in 16-8 stainless steel. Cr interference was a problem when the Si 2881 line was used. The effect was investigated for different source parameters. The minimum effect was obtained with the a-c arc. On the basis of more recent experience the Si 2516 line should be used unless Mo interferes. Mo interference is mainly a problem in high-speed steels.

b. At this period, cooperative testing further proved that there appeared to be no advantages in operating a spark source at high peak currents and single sparks per half cycle over multiple sparks of lower peak currents.

This source unit remained at the Universal Cyclops Plant in Bridgeville, Pa.

5. Aluminum Company of America Source Installation, January 27, 1948

The third trial source was a temporary installation at Alcoa research laboratory in New Kensington. At this location the L and N source was compared with the ARL high-precision source, arranged so that either could be used with the quantometer. The report contains a table of source parameters, running times, quantometer readings and line-to-background ratios. The conclusions were:

a. Precision and sensitivity for the two sources were comparable (and optimum) when the 350- μ h and residual resistance parameters of the ARL source were used. For these parameters the L and N source functioned best with 3/8-inch-diameter tungsten electrodes in the air interrupter.

b. The total gap energy (analytical plus interrupter) in the point-to-plane technique with the high inductance-low resistance parameters was about 550 watts, more than twice the energy required in steel analysis with pin samples. This source unit was later acquired by the Vanadium Corporation of America and is at present at their plant in Cambridge, Ohio.

6. A Study of Spectrochemical Reproducibility with the Air Interrupter Spark Source, March 23, 1948

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This is a progress report on the air-interrupter source in steel analysis employing the photographic technique. The main points in the report were: (1) analytical curve shifts were shown to be related to changes in the peak current for relatively constant gap energies and sufficiently large differences in the line pair excitation energies; (2) a considerable amount of photographic data in the report appears to contain more statistical information than computed in the report.

Some of the data from this report plus a discussion of the air-interrupter spark and spark-initiated arc sources were the subject of a paper presented at the Optical Society meeting held in Detroit in October, 1948. The paper was published in the J. Opt. Soc. Am., 39, 298 (1949).

7. Spectrographic Source Parameters for Western Cartridge Copper Alloys (Project M866), July 7, 1950

This short report from the Western Cartridge sponsored project deals with excitation studies made with the Leeds and Northrup project (M567) equipment at the University of Michigan. It includes a table on excitation parameters for a variety of copper alloys. The unusual thermal properties of copper and its alloys presented two problems: (a) The total gap energy with pin-type samples was even higher than in the point-to-plane technique for aluminum. The tungsten electrodes in the air interrupter did not stand up and were replaced with 3/8-inch diameter pins of a tungsten carbide alloy. (b) The radiation intensity was observed to be quite sensitive to the thermal capacity of the sample electrode holders.

At Western Cartridge, East Alton, Illinois, this source is still operated with the excitation parameters listed in the report. On November 21, 1952, the writer visited the Western Cartridge Laboratory at their request to check repeated failure of certain electrical components. The difficulties were located (faulty operation induced by a change in supervision) and reported by letter to Dr. William Gray, of the Leeds and Northrup research department.

8. Application of Direct Recording Methods to the Study of Spark Source Excitation Parameters in Spectrochemical Analysis of Steel, June 18, 1951

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2. Photo-Tube Currents and Radiation Signal Strength
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2. Analytical Gap Spacing
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4. Internal Standard

At this point the emphasis in our program had been shifted from sources for the photographic technique to the complete direct reader. The first direct-reading spectrochemical analyzer had been built at Leeds and Northrup and was being tested there prior to its trial installation at Universal Cyclops in August, 1951. In the report the important points are as follows: (a) an outline is presented of the "bread-board" arrangement of optics and photo-electric recording system set up at the University of Michigan; (b) ratio and intensity recorder curves show the short-duration stability in the photomultiplier detector, the preamplifier, the source, and the different radiation signals; (c) ratios of element line to internal standard line, or to overall light are investigated for extreme changes in excitation parameters; (d) it is concluded that the overall light stabilizes a ratio for all sorts of changes in excitation, and does this as well as an internal standard line (this is important since stability is required and in the scanning spectrometer only the overall light reference signal is available); (e) the intensity ratio for stainless steel, pin-type samples is shown to be very sensitive to small changes in source inductance.

9. Analysis of Steels with the Scanning Spectrometer, October 2, 1951

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1. Low Alloy Steel
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The important points considered in this report are as follows: (a) an analytical approximation is derived to show that integration time for scanning a line with the spectrometer is at most a few tenths of a second, although the single-line scanning time is 4.5 seconds; (b) in high-alloy-steel analysis, characteristic radiation for some of the elements cannot be isolated with our quartz prism spectrograph nor the scanning spectrometer; (c) the degree of element interference is demonstrated for both instruments and compared with the expected values computed from the concentrations and MIT line intensities; (d) computations are carried through to show what corrections can be made when interfering elements are present; (e) some of the standards consistently do not fall on the curve which has since been interpreted as the failure of the overall light to satisfy the internal standard requirements.

10. Internal Standard Properties of Nondispersed Selective Filtered Radiation, (Pittsburgh Paper) March 6, 1952

This paper, not published, is based on some of the work from the June 18 and October 2, 1951, reports. The paper presents data on the relative merits of the internal standard signal when this is a single line, total non-dispersed, or nondispersed-selective filtered radiation. It is pointed out that Cr in steels affects the intensity of non-dispersed radiation. As a result such signals cannot be relied upon as internal standards. All three types of signals, however, are shown to be similarly effective as reference signals for stabilizing ratio fluctuations due to the source.

11. Low Alloy Steel Working Curves for an Integrating Type vs. a Scanning Type of Direct Reader, December, 1953.

This is a short report comparing the working curves for a common set of standards that were run on a Baird (River Rouge Plant, Ford Motor Company) and the L and N (University of Michigan) direct readers. The report includes fairly complete information on the procedure and parameters that were used. The curves are shown for Si, Mn, Cu, Mo, Cr, Ni, and V. Two facts are emphasized in this work: (a) the precision obtained with the short time integration (L and N) instrument is as good as with the longer integration (Baird) instrument; (b) the L and N instrument does not require the rigid room-temperature control that the fixed exit-slit instruments require.

B. GENERAL SUMMARY1. Source Studies

The early work on sources, starting in 1944, has been fully outlined in the preceding sections from the progress reports and papers. The major contributions are once more summarized as: (a) a new air-interrupter design and complete elimination of the synchronous interrupter; (b) establishing the power requirements so that the electrical components have the proper rating; (c) introducing a spark-initiated a-c arc which eliminated expensive duplication in a number of electrical components already required in the spark circuit; (d) introducing electrical instrumentation for measuring parameters needed in specifying source operation; (e) setting up a photoelectric means with a quartz prism spectrograph for the purpose of observing the radiation more directly than is possible with the photographic technique; (f) cooperating in a number of the Leeds and Northrup built source installations in laboratories employing the photographic technique.

2. Direct Reading Studies Prior to the L and N Spectrochemical Analyzer

During this phase of our project work the photoelectric recording equipment described in the June 18, 1951, report was used to investigate a number of factors pertinent to the design and operation of the scanning-type direct reader that was being built at Leeds and Northrup. The results from this work are included in the preceding reports or papers and can be briefly summarized as follows: (a) the selection of a radiation band as reference signal for the ratio measurement with the scanning-type monochromator; (b) the determination of excitation parameters (for spark source and samples) that would result in the best possible time-of-wait curves (smallest peak-to-peak fluctuations and a constant average); (c) for a variety of ferrous alloys, a demonstration shows that a normal change in some of the parameters results in a change in the general shape of the intensity curves, while a change in others affects primarily the magnitude of the intensity; (d) a comparison of the relative contributions from the statistical properties of the photomultiplier tubes and the radiation source for decreasing signal-to-dark current ratios; (e) the results from d suggested that fluctuations in the radiation intensity originating at the source were effectively reduced by our line-to-reference-band ratio-measuring technique and that one should work with spectral intensities which had a signal-to-dark current ratio of at least 10:1.

3. The L and N Spectrochemical Analyzer

The work that has been done in our laboratory with this instrument is summarized in a paper presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 5, 1954. Since the paper has not been published and most of the data were compiled after the last progress report (December, 1953), it is included with this report.

There are several points related to the operation of the instrument which may not have been clearly stated above or in the paper that follows. They are:

a. In our present method of scanning, the quantitative reading represents a very short integration time (Progress Report, Oct. 2, 1951). The precision of the method is dependent on the stability of the line-to-reference-band ratio. An on-the-line ratio record of these two quantities becomes increasingly unstable with increasing discharge circuit inductance. For pin shape samples, 7/32-inch in diameter and coned to 130° included angle, the effect becomes intolerable when the inductance is increased much past 25 microhenries. The trouble could be partly in the optics, because in this range of increasing inductance the discharge cross section increases considerably. The other effect is probably differential evaporation.

b. Differential evaporation for solid samples, pins or flats, causes even larger line-to-overall-light ratio fluctuations with a-c arc excitation. With the arc, the average of at least three readings seems to be necessary. This investigation should be continued further.

c. With the photographic technique during a study of solution analysis the precision came out to about the same for all methods of excitation, and was similar to that obtained for the low-inductance spark with metal pin samples. With the direct reader, precision studies were not as complete, but also appeared more uniform from source to source. In solution analysis for arc excitation, the unidirectional source is used, with the counter electrode as the anode. For straight a-c arc operation the solution is blown from the porous cup when the current exceeds about 1 ampere.

PHOTOELECTRIC SINGLE CHANNEL

MEASUREMENTS IN EMISSION SPECTROSCOPY*

Present day quantitative measurements in emission spectroscopy employing either a photographic or photoelectric recording technique are based largely upon the internal-standard principle first proposed by Gerlach.¹ In this method the percent concentration of an element is derived from the intensity ratio of two lines. The radiation intensities of the two lines are simultaneously recorded as integrated values during the exposure time of so many seconds. The analytical line is of the unknown element in the matrix and the internal standard line is of an element whose concentration is either known or can and must be determined first.

Gerlach proposed the two lines should be a homologous pair. That is, the two lines should have similar excitation energies and would therefore respond alike to fluctuating excitation conditions in the source. The photographic method also prefers that the line pair be close together in the spectrum, which often makes it difficult to find homologous lines. In modern direct readers with fixed receivers, it is common practice to employ but one reference line for all the different elements to be recorded, which again means that the homologous line pair selection is not followed. In all practical cases both methods yield satisfactory results. Maintaining a constant ratio of evaporation for the unknown element with respect to the reference element appears more important than the selection of line pairs having identical excitation potentials. Or, if as in the case of total radiation a frequency band is selected in which all lines and continuum are functions of the sample vapors only, and not for example include appreciable radiation from the atmospheric gases, the vaporization requirement will have been met. In an unpublished paper presented by the author at this conference in 1952, it was shown however that the radiation intensity of a band might be seriously influenced, for example, by the Cr concentration in low alloy steel.

In general therefore the internal standard line serves a two fold purpose. It must stabilize the measured radiation of the analytical line with respect to fluctuations during the excitation of any one sample. Its second function is to furnish a reference radiation between samples. The proposed single channel method employs two signals with the one automatically cancelled from the recorded measurement.

* Paper presented at the Pittsburg Conference on Analytical Chemistry and Applied Spectroscopy, March, 1954.

The disadvantages of multichannel systems are well known and were recently enumerated by Brehm and Fassel.² Direct reading instrumentation based on a two channel ratio measurement does somewhat reduce the need for source stability, but demands greater stability of the detecting system. Photomultiplier fatigue and thermal shifts require frequent standardization, and closely regulated room temperatures. By comparison the single channel method is relatively insensitive to changes in the detecting system but requires greater care in excitation.

1. The Single Channel Method

An alternate procedure to multichannel simultaneous integration is single channel successive integration. The instrument for which this method has been worked out is the Leeds and Northrup Direct Recording Spectrochemical Analyzer. The three basic components of this instrument are an air interrupter controlled, high voltage spark and 60 cps spark initiated a-c arc source³; an Ebert plane grating monochromator of the type described by Fastie⁴; and a two photomultiplier tube-dual channel preamplifier-ratio recorder system.

The monochromator is a scanning type instrument with N possible fixed grating positions. Each grating rotation is chosen to position a given spectrum line near the exit slit. The line is scanned across the exit slit by a lateral motion of the entry slit. The first line that is scanned is of the internal standard element, thus leaving N - 1 grating stops for unknown element lines. In this instrument, Figure 1, radiation from the source falls upon a quartz plate located in front of the monochromator entry slit. A small portion of the radiation is deflected through 90°, passed through an absorption filter (transmission band 2300-4000 Å) and converted into an electrical signal by the photomultiplier tube P_r. The radiation passed by the quartz plate and the entry slit is collimated, dispersed and then focussed on the exit slit of the monochromator. Behind the exit slit is a second photomultiplier tube P_x which converts the incident monochromatic radiation into an electrical signal. The two signals are then amplified in the dual channel amplifier and recorded as a ratio $R = I_x/I_r$.

In an actual sample analysis run the internal standard line to reference band ratio is recorded during the preexposure-time. During this period the reference line is repeatedly scanned and the x-channel output is adjusted until the recorded ratio reading is 100. The individual element lines are then scanned in succession without changing any of the instrument settings, except that different predetermined voltages are applied to the x-channel phototube for the scanning of each line. These voltages are fixed values, chosen earlier to set the concentration ranges of the instrument.

The line to reference band ratio can be expressed as

$$R_a \approx \frac{I_{xa}}{I_{ra}} = \frac{J_a k_x P_{xa} A_x}{J_r k_r P_r A_r} \quad (1)$$

where I_{xa} and I_{ra} are the electrical input signals to the ratio recorder, J_a is the a line and J_r the reference band radiation intensity, k_x and k_r are the respective photomultiplier tube constants (fatigue, etc.), P_{xa} and P_r are photomultiplier tube amplification constants (functions of the applied voltages), and A_x and A_r are the dual channel amplifier gain constants. If the ratio R_i of an element line is divided by R_a of the internal standard, line the result can be expressed as

$$R_i = R_a \frac{J_i}{J_a} = K \frac{C_i}{C_a} \quad (2)$$

Where K is a constant since R_a can be set to read the same for all samples, and C_i and C_a are the unknown and internal standard element concentrations, respectively.

In the above derivations a linear relationship between line intensity and element concentration has been assumed. This same assumption has been made below, where all analytical curves are plotted to show concentration ratios. Effects of background or self absorption have not been considered.

2. Excitation Requirements

In the single channel method it is best to choose the excitation parameters so that all line to reference band intensity ratios are constant during the exposure time. To what extent this has been possible to achieve is illustrated in Figure 2 for stainless steel pin samples, and in Figure 3 for the porous cup solution technique. The solutions were 25% H_2SO_4 acid, containing 20 mg per ml of titanium and several other metals at considerably lower concentrations.

The stainless steel curves show the important effect of the inductance. Increasing the inductance in this range tends to increase the sampling area. As a result, local overheating aggravated by poor thermal conductivity of stainless steel, can be effectively reduced. Low alloy and tool steel curves are less difficult to stabilize.

Figure 4 shows from right to left 6 repeat scannings of the Fe internal standard line followed by 13 consecutive runs over the Mn line. For photographic reasons this data was taken on special recorder paper and the settings were made so that the Fe line reading would be just under 100. In

an actual analysis run the Mn line would of course be scanned only once. The percent deviations tabulated below the figure are an example of the reliability of single readings from a given analysis run.

3. Precision and Sample Inhomogeneity

A precision test has been run by the single channel method and compared with photographic integrated results. In this test 56 alternate single determinations were made by each method for the same pair of low alloy steel pins. The pins were machined to a 130° cone and truncated to about 1 mm before each exposure. In Figure 5 the individual Mn determinations are shown graphically for the first 21 alternate exposures by each method. The two methods had in common only the sample, the excitation parameters to which each source was set and the preexposure time of 40 seconds. It is apparent that Mn segregation in this sample is a major cause for the individual deviations from the nominal concentration of 1.95%.

Similar curves were prepared for 0.175% Cr and 0.35% Si in this sample from the same series of exposures. For these segregation was not so apparent, in particular the Cr deviations fluctuated more or less at random.

TABLE I

Percent Concentration		Standard Deviation	
		Photographic	Photoelectric
Mn	1.95	1.89	1.74
Si	0.35	2.24	2.39
Cr	0.175	2.03	1.50

Standard deviations based on the 56 determinations by each method are tabulated in Table I. The data was taken on 8 occasions over a one month period. On each occasion 7 exposures were taken by both methods, since this was the number of exposures to go on one photographic plate.

4. Analytical Curves

In this section analytical curves obtained by the single channel-scanning method are compared with curves from simultaneous intergration data. The same standard samples were used for the two methods.

The curves in Figure 6 are for Cr in low alloy steel. Along the vertical in the center of the figure the numbers identify the samples. The upper curve was plotted by moving the vertical scale up one cycle on the logarithmic scale. In this way the full range can be shown on two cycle paper. The 17 samples were run twice by each method, with a time interval of about 10 days between the two runs. A very definite curve shift at the left indicates instability of the two channel ratio technique over the ten day period. The single channel data at the right shows no shift. It is here important to note that in the Randall Laboratory of Physics, where the scanning instrument is located, there is no air conditioning. Mainly due to prevailing weather conditions the room temperature on the two occasions when the scanning data was taken differed by about 10°F.

Four months after the data of Figure 6 was taken, the same samples were again run by the single channel method. The long-time stability of the working curves by this method is illustrated in Figure 7. Here the original lower right hand curve from Figure 6 was plotted without showing any of the individual points. The points in Figure 7 are single determinations from the later run shown superimposed on the original curve. This same curve stability was obtained for Si, Mn, Ni, Mo, and V, the other elements scanned during these tests.

The Cr curves based on six stainless steel samples are shown in Figure 8. In this case the curve at the left was obtained by the usual photographic procedure. The linear ratio recorder readings for the curve at the right were converted to a logarithm scale and plotted as shown. The two curves differ mainly in their slopes. These could be matched by reducing the amplification in the x-channel of the photoelectric instrument. The standard deviation for Cr in the six samples was determined as 1.5%, the same as for low alloy steel. This figure is based on 42 determinations, 7 for each of the six samples.

The single channel method has also been tried with the porous cup-solution technique. In this work synthetic standard solutions were prepared for titanium metal analysis. The 5 standard solutions from which the curve of Figure 9 were prepared contained the Mn to Ti ratios as shown. In addition these solutions contained the same Cr, Al and one half the Fe to Ti ratios. The solutions were mixed to contain a total metal content of about 20 mg per ml in a 25% H₂SO₄ solution. A standard deviation of 0.90% for Cr and 2.54% for Al was computed from 20 determinations of a titanium alloy containing 5.12% Cr and 3.45% Al. For the same alloy solution the standard deviations from 10 photographic determinations were 1.45% for Cr and 3.14% for Al.

5. Summary

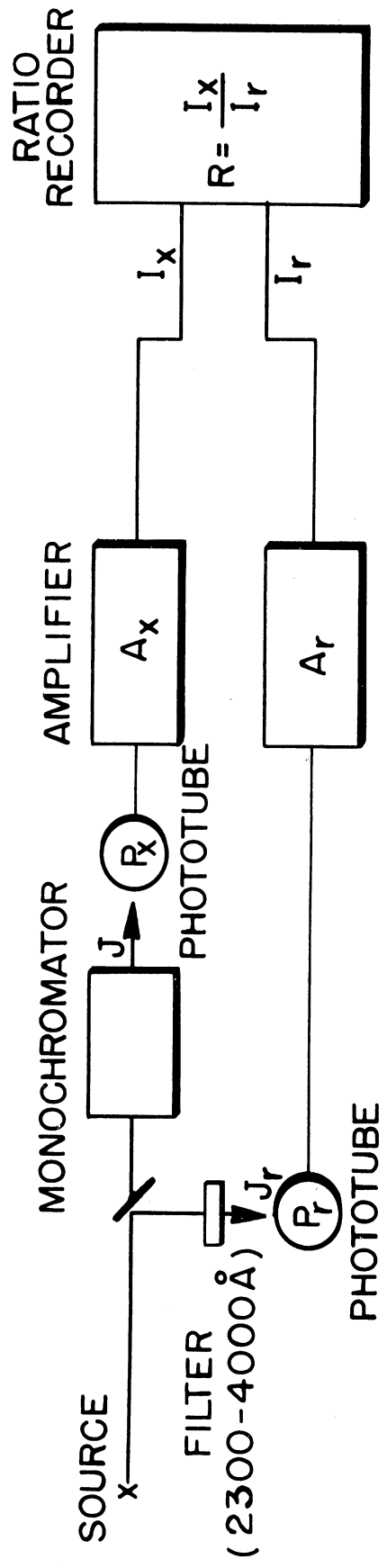
The single channel scanning method as here proposed has been shown to give analytical results comparable to photographic or other direct reading simultaneous integration methods. The basic idea is to measure N successive line to reference signal ratios, the first of which is the internal standard line and on which the instrument is standardized. In this way the reference signal serves only as a stabilizer for the instantaneous intensity fluctuations and is essentially eliminated from the recorded data. The internal standard line retains its usual function of correlating relative intensities between samples.

This report has been confined to data taken with a high voltage spark excitation. Of the atmospheric discharges, it is probably the most advantageous source to the single channel method. The a-c arc has only been tried briefly with metal sample electrodes. The radiation intensities and ratios tend to fluctuate considerably, due to differential evaporation perhaps. In solution analysis with the a-c arc the fluctuations are less difficult. Additional work needs to be done to make this method applicable to trace analysis.

The work done at the University of Michigan in this field has been done in the Department of Physics under the auspices of the Engineering Research Institute. The Leeds and Northrup Company of Philadelphia has been the sponsor. The generous cooperation received from the members of the Leeds and Northrup research laboratory has been very valuable and is hereby acknowledged.

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$$R_a = \frac{I_{xa}}{I_{ra}} = \frac{J_a k_x P_{xa} A_x}{J_{ra} k_r P_r A_r}$$

$$R_i = \frac{I_{xi}}{I_{ri}} = \frac{J_i k_x P_{xi} A_x}{J_{ri} k_r P_r A_r}$$

$$R_i = k R_a \frac{J_i}{J_a} = K \frac{C_i}{C_a}$$

Figure 1 Block diagram of spectrochemical analyzer for single channel ratio analysis.

Cr-2877
2300-4000

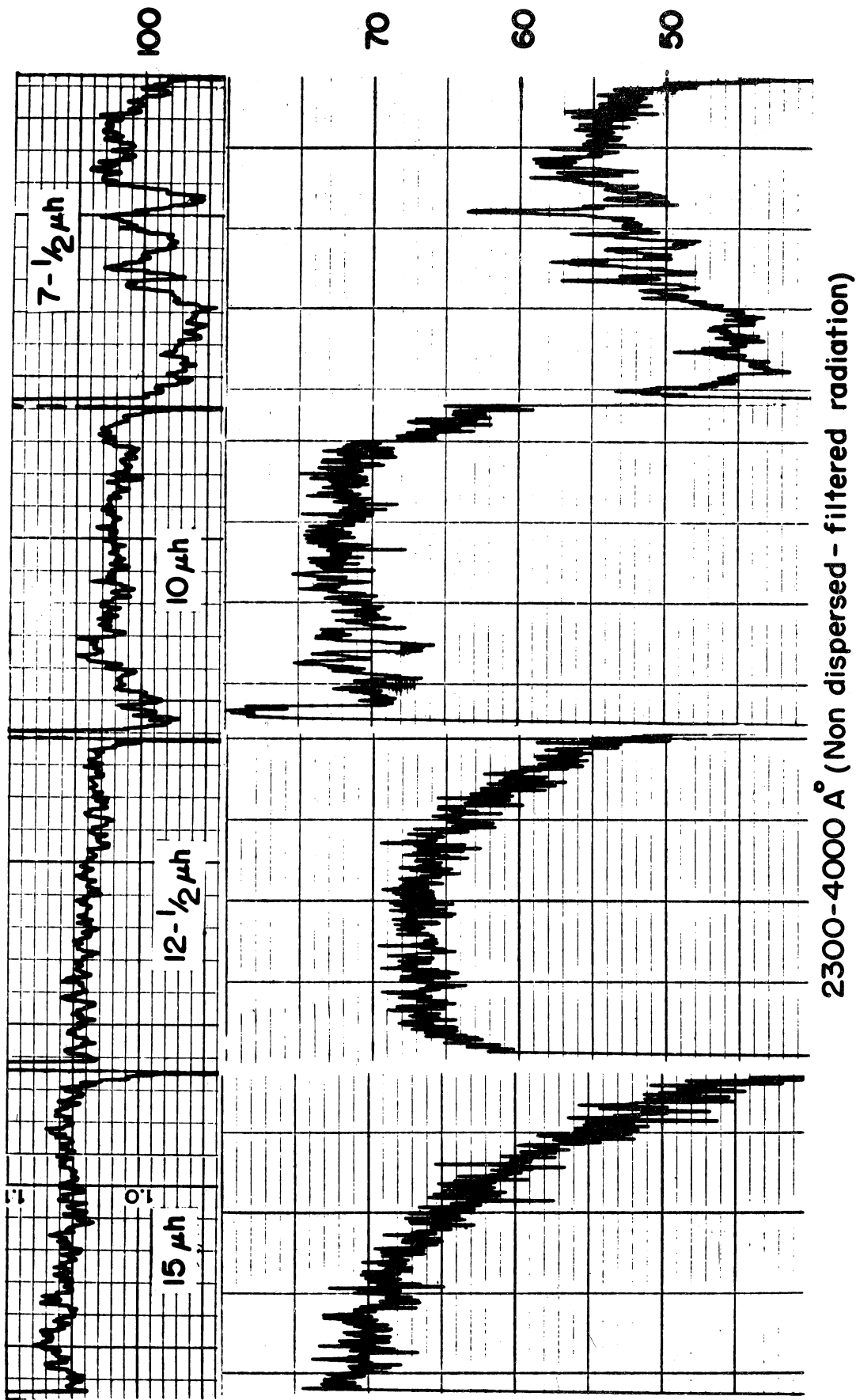


Figure 2 Simultaneous recorded ratio at the top and reference band intensity below, for four different spark circuit inductance values. Stainless steel (18.75% Cr) 7/32 in. D pins, 140° cone, 4 mm gap. 60 sec. runs, without preexposure, time right to left.

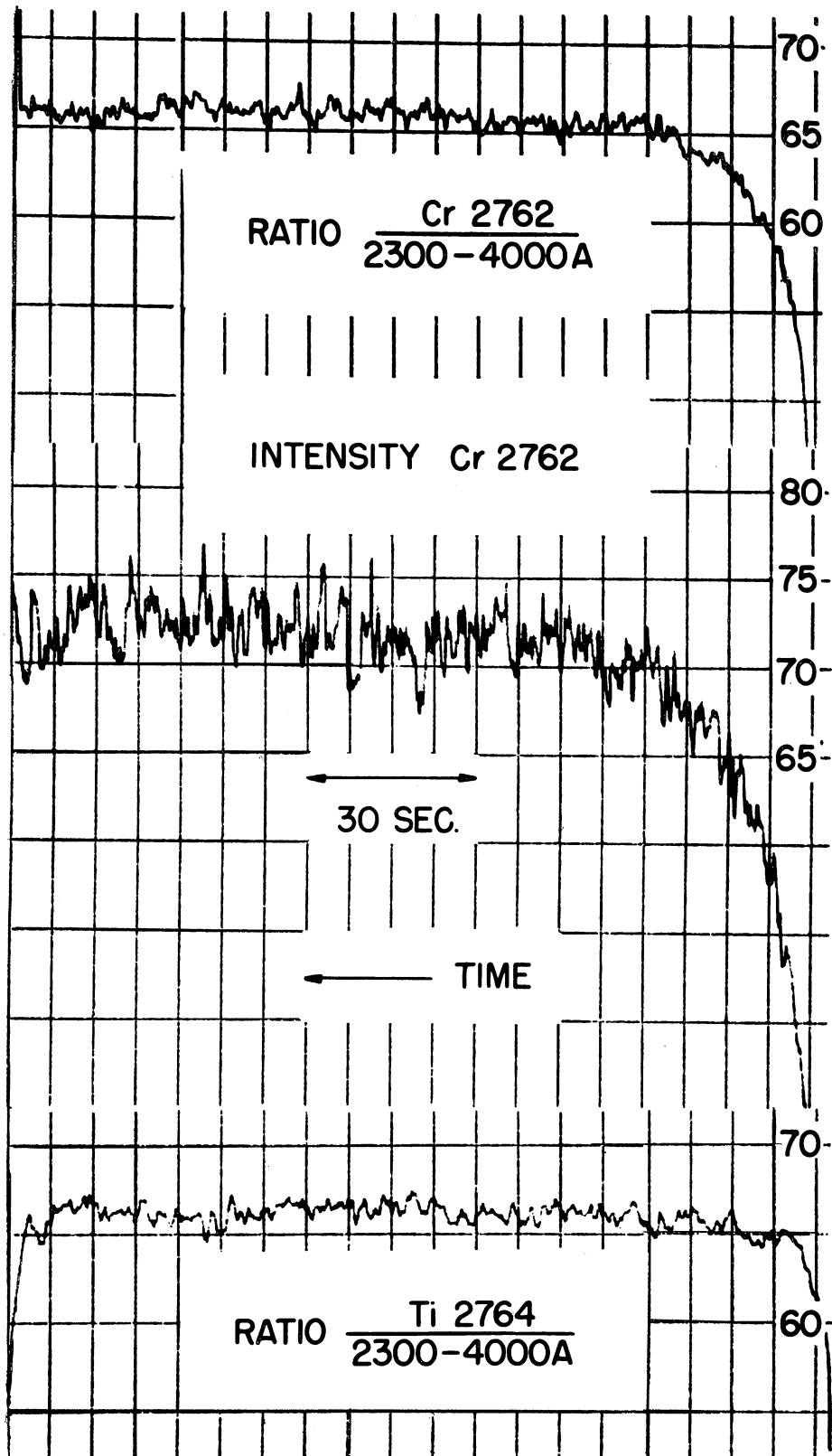


Figure 3 Direct-recorded time-of-wait curves for porous-cup-solution technique for spark source parameters of .002 μf , 15 μh , 1.1 ohm, 15.5 k.v., 480 sp. per sec. Full scale reading is 100.

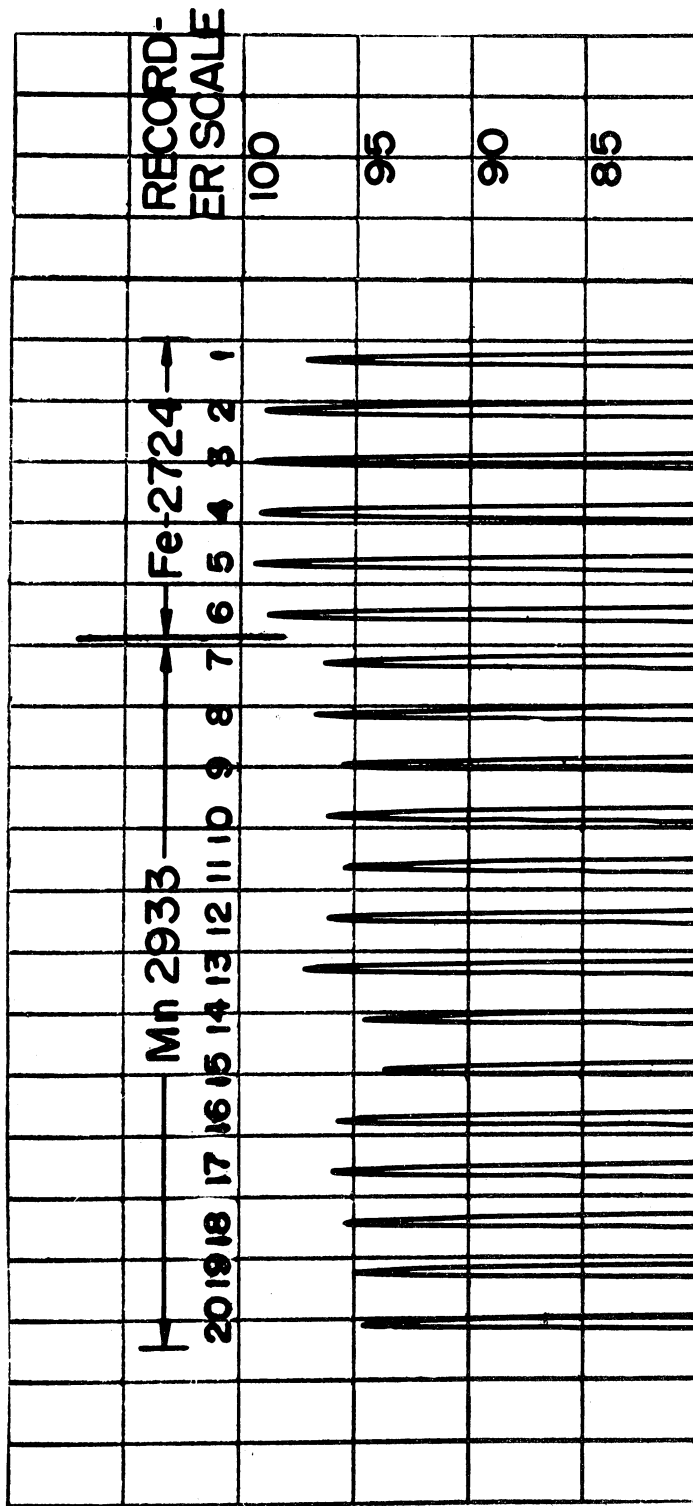


Figure 4 Single line scanning. Ave. Mn conc. = 1.95%, stand. deviation = 1.05%, max. deviation = 2.15%. Time right to left time for single scan is 6 sec.

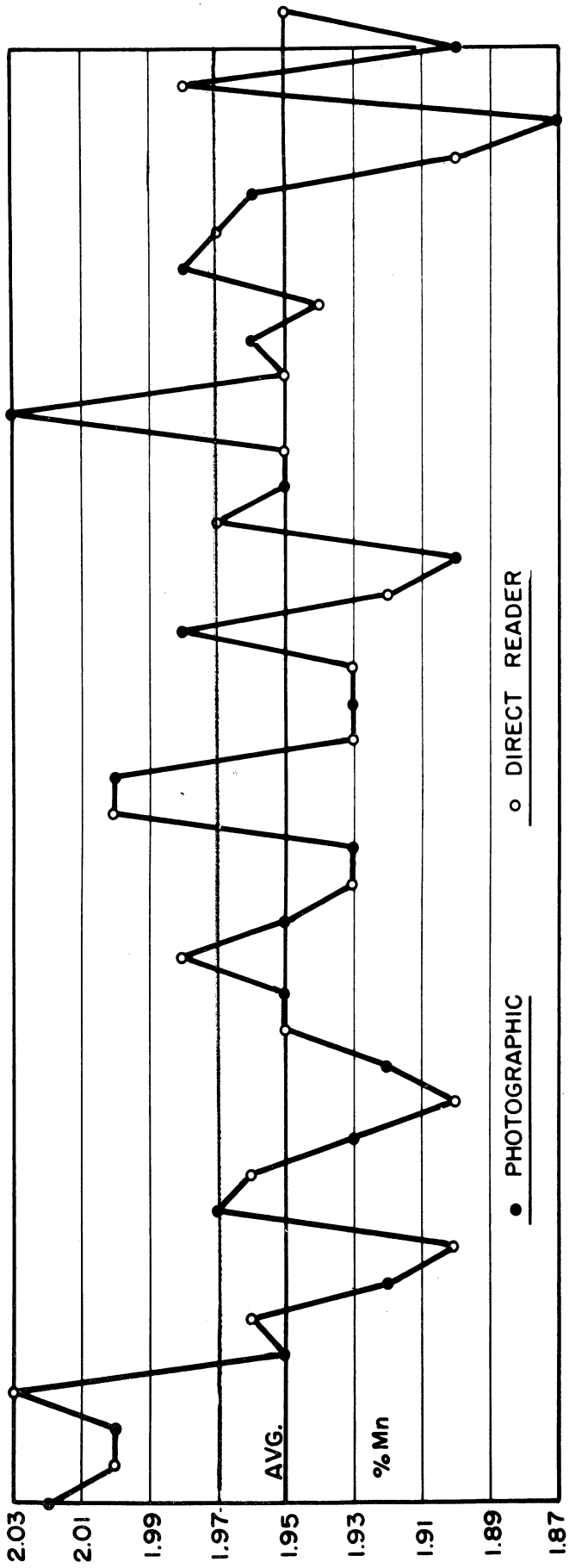


Figure 5 Alternate photographic and direct reading Mn determinations in alloy steel, nominal concentration 1.95%.

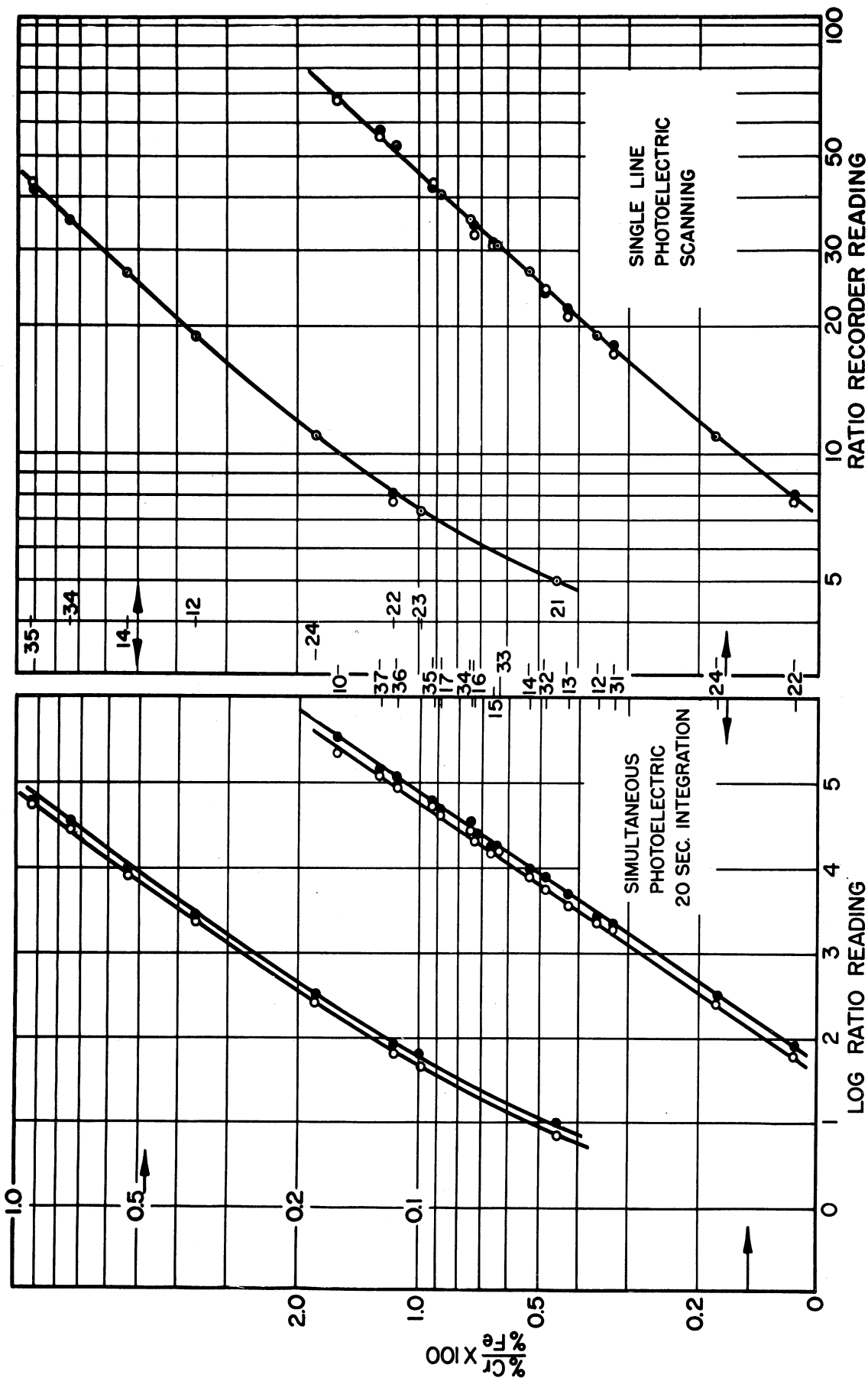


Figure 6 Working curves for Cr in low alloy steel by a standard direct reader at the left and by the L. and N. scanning instrument at the right.

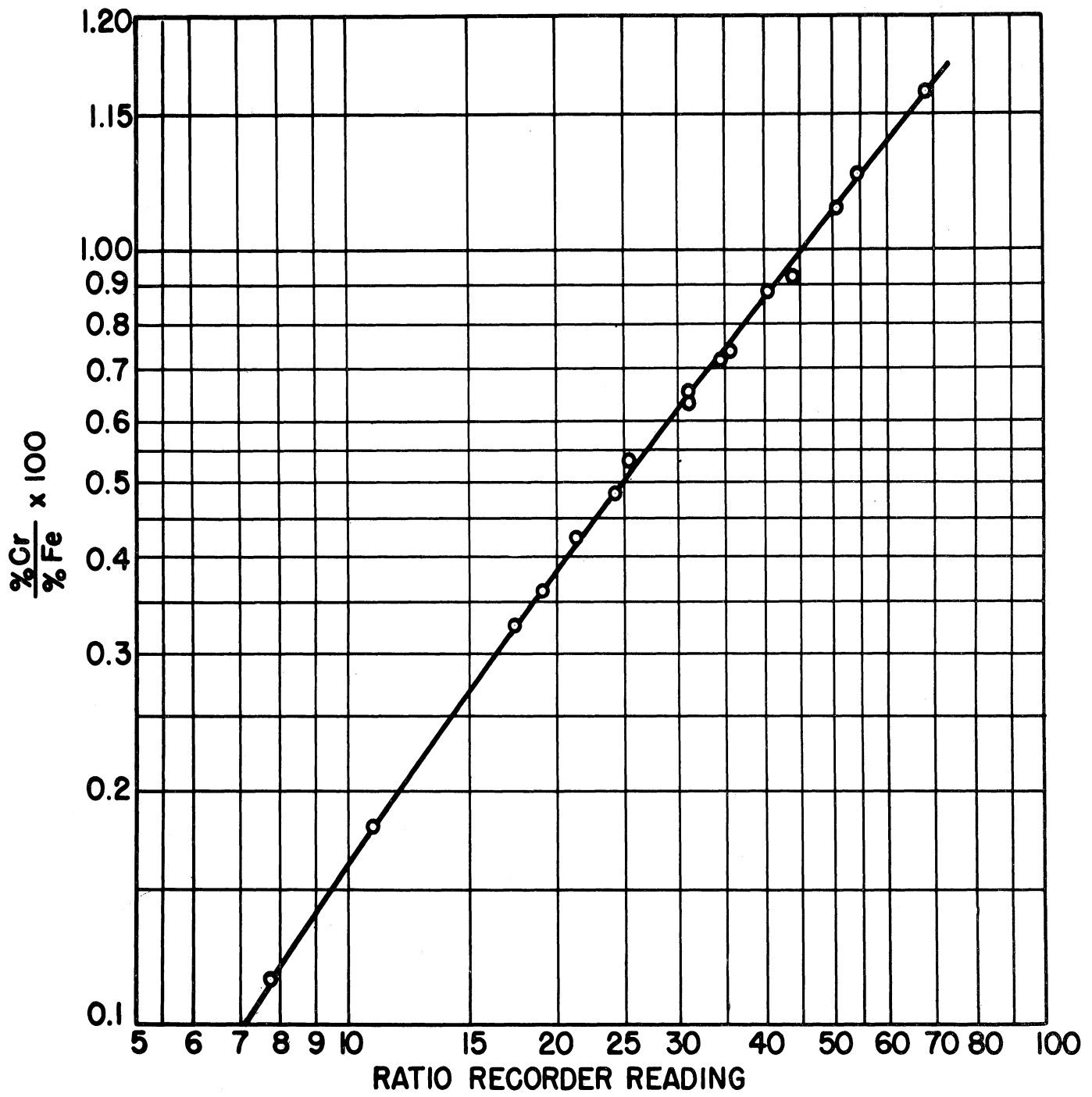


Figure 7 Working curve stability shown by superimposing single analysis point on a four months old curve.

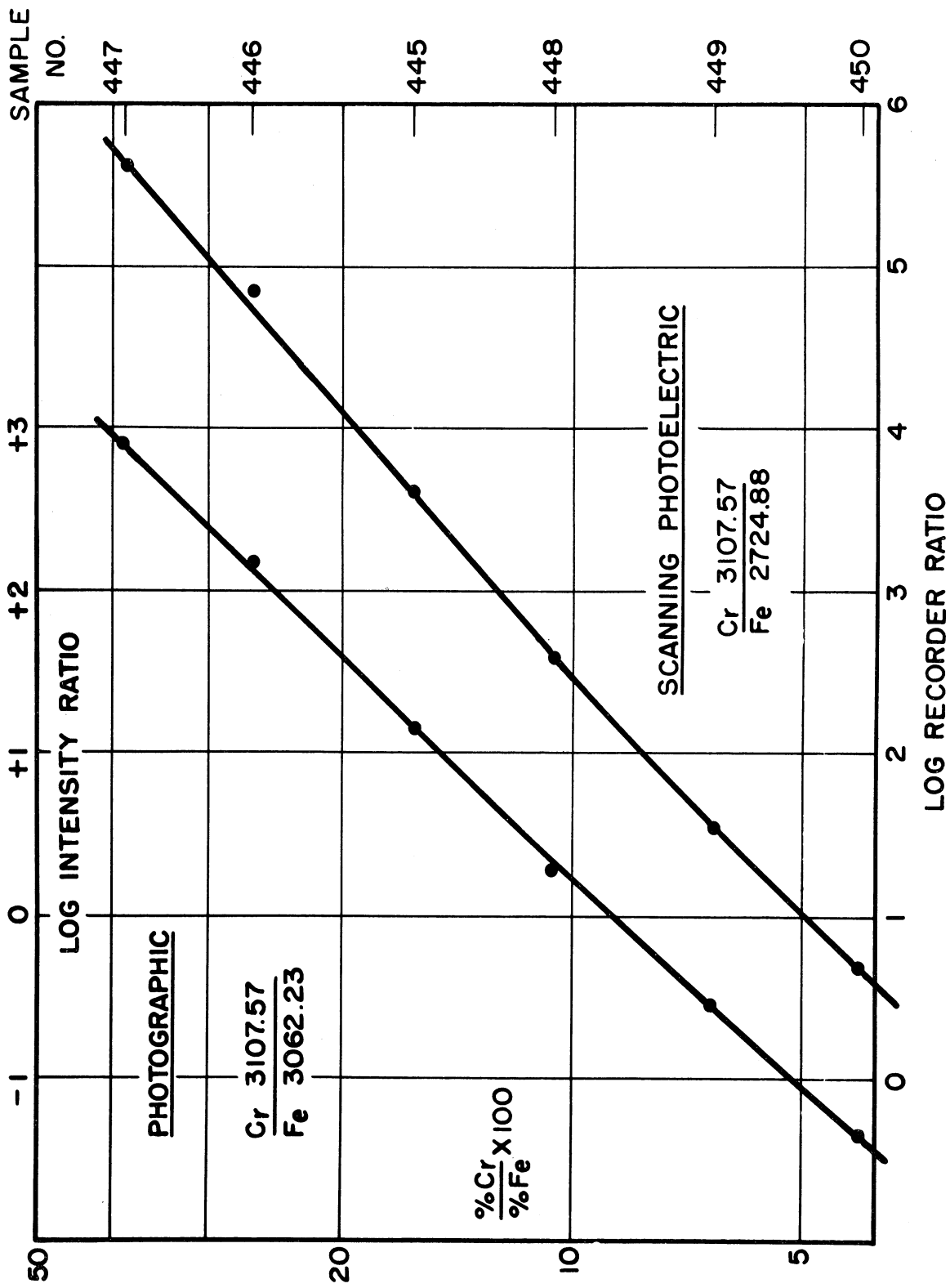


Figure 8 Analytical curves for Cr from six stainless steel-pin samples.

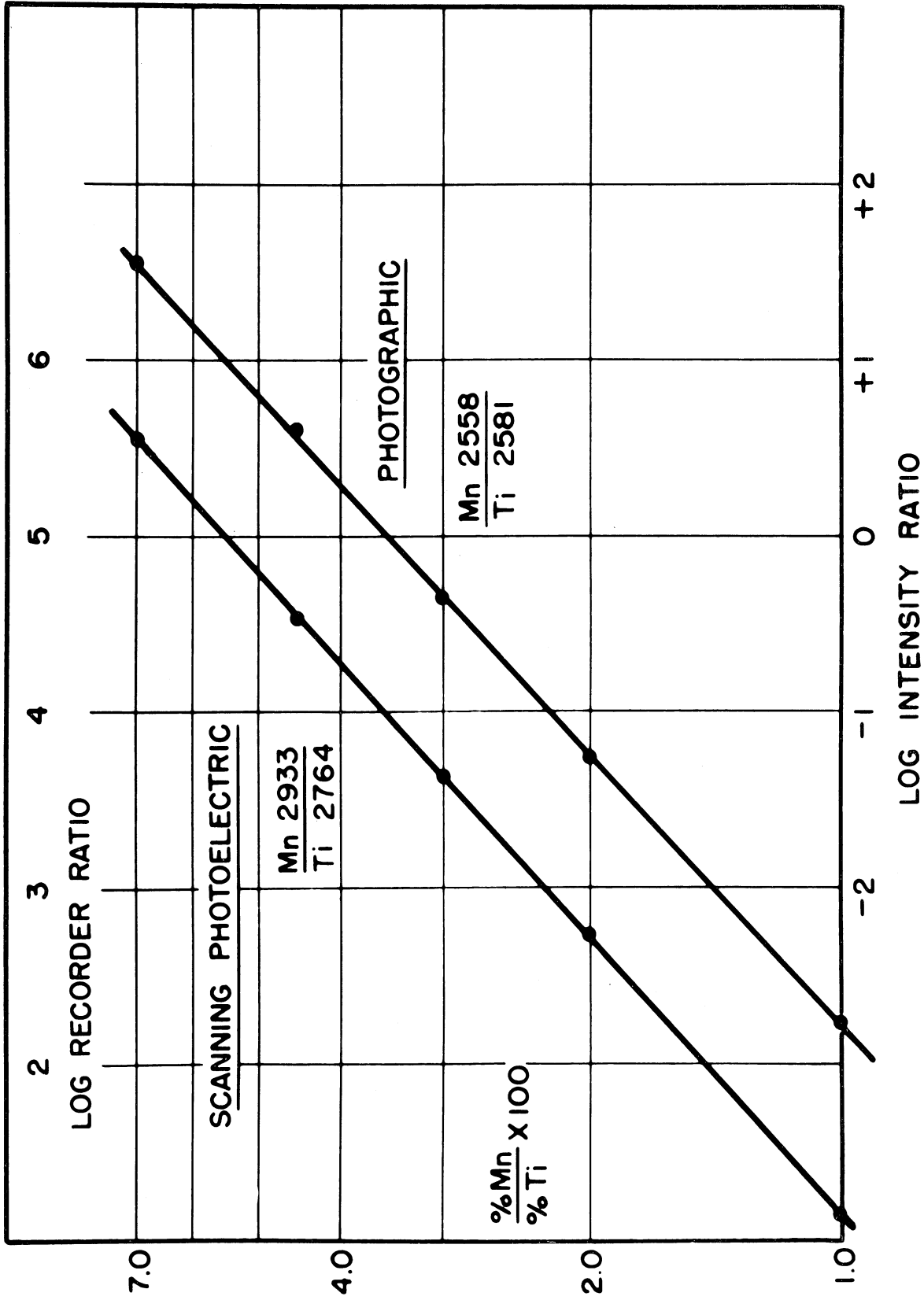


Figure 9 Mn working curves from Ti synthetic standard solutions by the porous cup technique.

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