

Spectrochemical Analysis of Sheet Steel at the Great Lakes Steel Company

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Introduction

IN an earlier number of this journal,¹ the authors described a spectrographic laboratory at the plant of the Campbell, Wyant and Cannon Foundry Company of Muskegon, Michigan, for the rapid and accurate analysis of alloy cast iron. In this installation and in one at the River Rouge plant of the Ford Motor Company,² more recently described, the alloying materials in the irons handled are present in amounts ranging up to 4 percent; the problem was thus one of determining composition rather than of checking purity. The procedure was designed not for high sensitivity and low concentrations, but for speed and precision in composition ranges somewhat higher than is usual in spectrographic analysis.

More recently a spectrographic installation has been completed, for the Great Lakes Steel Corporation of Ecorse, Michigan, to serve a quite different purpose. This company manufactures, among other products, sheet steel for automobile bodies. The sheet is rolled, usually to 20 gauge thickness, from "rimming steel" billets of low alloy content, such content coming chiefly from the scrap steel, which is added to the melt. In the manufacture of automobile-body parts, such as fenders, hoods, or tops, the sheet steel is drawn cold in huge stamping presses. Particularly for fenders, the draw is very deep, and the demands on the properties of the steel consequently severe. Proper heat treatment and mechanical working of the steel can aid greatly in attaining the desired properties. It is believed, however, that the presence of alloy metals in the steel, even in the amounts found, which are as low as a few hundredths of one percent, may have significant and often harmful effects upon the drawing properties of the steel.

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Chemical analyses of iron for such small percentages are time-consuming and attain the required precision only with difficulty. It was, therefore, proposed to undertake these analyses spectrographically. The spectrograph seemed ideally suited for such a task, since the sensitivity of arc sources is much greater than the present requirement, and much greater than can ordinarily be attained chemically.

As pointed out, however, in the earlier article, sensitivity is not the only requirement of a light source for quantitative spectrographic analysis. The source must be consistent in operation, so that, in successive spectra from the same sample, the spectral lines of the various constituents of the electrodes shall have the same relative intensities. The problem of the analysis of body sheet steel resolves itself, fundamentally, into the selection of a light source of the requisite sensitivity and reliability.

The Light Source

Studies of light sources for iron analysis have shown that the small arc on 220 volts, though sensitive, is quite unsatisfactory. Surface oxidation, subsurface boiling of the electrodes, and random wandering of the cathode spot result in erratic fluctuations of electrode and arc temperatures, with consequent variable and differential rates of evaporation and of excitation of different components of the electrodes. The accuracy of iron analyses performed with the d.c. arc is therefore poor, although the sensitivity to small concentrations of foreign metals is high. On the other hand, the spark circuit used in the cast iron analysis gives a source of high accuracy but not of sufficient sensitivity for the present application.

After tests of several light sources, a high voltage alternating-current arc was chosen for the present installation. In this type of arc the secondary of a high voltage transformer is connected to the arc through a large ballast resist-

ance, which controls the current. The current is usually 1 to 3 amperes, with potentials of 1100 to 4500 volts, and the gap is made short enough so that the arc can reignite at each half-cycle.

Observations of the arc with an oscilloscope show a nearly sinusoidal variation of the current, while the voltage (Fig. 1) shows peaks at the break, *D*, and at reignition, *C*, of the arc. The reignition voltage must at least equal the minimum sparking voltage for the given ionized gas and electrode material.³ Furthermore, it depends on the rate at which ions are lost from the discharge gap and on the duration of the quiescent period of the arc. Each new half-cycle starts with a breakdown, usually to a new point on the electrodes, and probably with some explosive release of electrode material. As the current rises, the initial glow discharge changes to an arc discharge, which persists, at the arc maintaining voltage *A*, until almost the end of the cycle, when, with falling current, the glow reappears at the higher voltage, *D*. The wandering of the cathode spot is controlled in that it is forced to re-establish itself at each half-cycle. The fluctuations of electrode and arc temperatures are much less than in a d.c. arc, and experimental results show that the a.c. arc is much more reliable than the d.c. arc for quantitative spectrochemical analysis.

The high voltage a.c. arc has been applied by Duffendack and Thomson and by others^{4,5} to the analysis of fluids and solutions; they used graphite electrodes on the tips of which a sample had been dried. As adapted to metallic electrodes in the present work the a.c. arc has marked advantages for steel analysis. The sensitivity is high and the consumption of material small, while the low current avoids collapse or dripping of the sheet samples. It is found desirable to mount the two sheet electrodes on edge at right angles to one another. The arc is thus localized at the intersection, and burns between two small spots which are cross sections of the sheet. Since the sheets are rolled down from rimming billets which are not uniform in composition throughout their sections, it is desirable to examine such a cross section of the sheet and to obtain its average composition.

The relative intensities of the spectral lines in the a.c. arc are affected by changes in arc current and in gap length. Optimum values must be

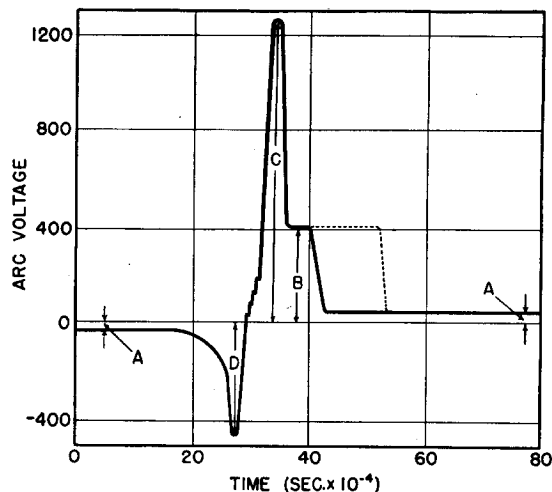


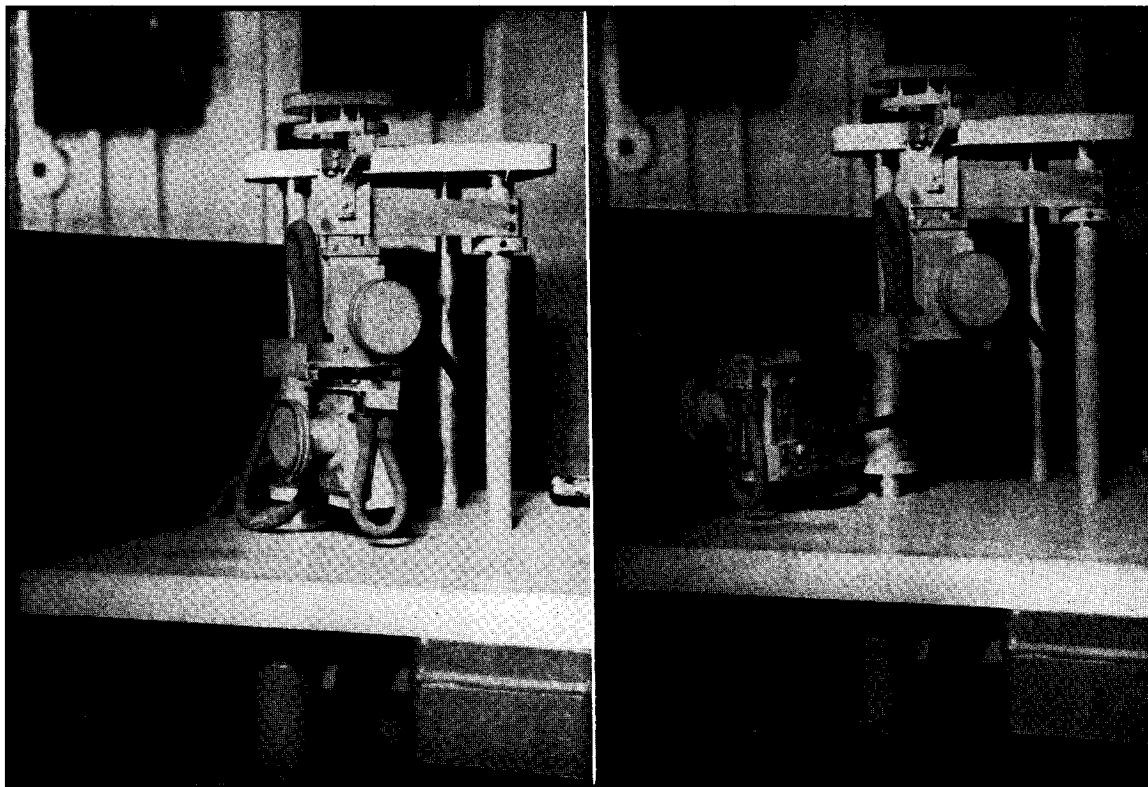
FIG. 1. Variation of voltage with time during one cycle of an a.c. arc. *A*, *A*=arc maintaining voltage, *B*=glow voltage at breakdown, *C*=sparking voltage at reignition, *D*=glow voltage at end of cycle.

determined experimentally and carefully reproduced in each exposure. Furthermore, the current used (1.5 amperes) heats the sheet electrodes sufficiently during an exposure to affect the relative rate of evaporation of the various components of the steel. Control of the sheet temperature by water cooling is essential to accuracy.

Instruments

For the Great Lakes Steel Company installation an arc stand has been developed which allows screw adjustment of the arc gap, and rapid mounting of the samples in water-cooled clamps. Fig. 2 shows two photographs of the stand—in operating position, (a), and with the lower jaw swung open for loading, (b). Wooden end plates connected by three metal rods give a rigid frame. Two of the rods carry the electrode clamps, which are electrically insulated by the wooden end plates. Rubber hose seen in the figure carries the cooling water to the four jaws. For convenience in loading, the lower clamp rotates, as shown in (b), on its supporting sleeve. The rotation is limited at its end of the swing by pin stops. The upper clamp assembly is rigidly fixed in position by set screws.

A sectional drawing of one of the clamps is shown in Fig. 3(a). The jaws are held by the screw, *C*, which is operated by a removable handwheel and are opened by the spring *D*. Two pins, *H*, serve to space the clamps. One of the



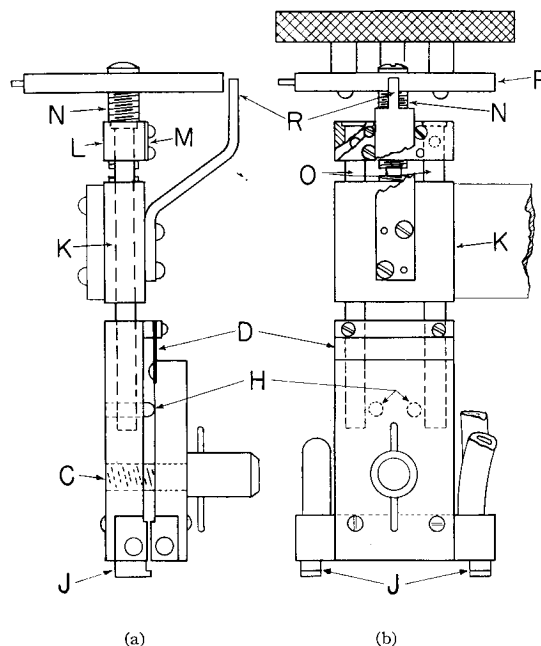
(a)

(b)

FIG. 2. Arc stand with water-cooled clamps; (a), in operating position, (b), open for loading.

water-cooled jaws carries at each end a gauge, *J*, which permits the sheet sample to project $\frac{1}{8}$ inch above the jaw-face. The sample is brought up against these gauges and clamped. Thus regardless of the width of the strip of sheet used, a uniform projection of the sample is assured. This uniform projection together with water-cooling of the jaws and the fixed current, gives the control of the sample temperature which has been found essential to uniform results.

Rapid and accurate setting of the arc gap is accomplished by the micrometer screw and friction clutch shown in Fig. 3(a) and (b). The screw, *N*, running in the supporting member, *K*, raises and lowers the bridge, *L*. The bridge, by friction of the spring, *M*, carries the two rods, *O*, which support the upper electrode clamp. A pin in the wheel, *P*, striking the stop, *R*, limits the rotation of the screw to that corresponding to the desired electrode gap. When the two clamps are loaded and in position, and the wheel set to lift



(a)

(b)

FIG. 3. Details of clamp assembly.

the clamp to its highest position, the upper clamp is pushed down by hand until the sheets touch. The handwheel is then turned to the other limit of its travel, and back to its former position. As the bridge moves downward, slippage occurs in the friction member; during the upward motion, no slippage occurs, and the electrodes are given a definite separation of $\frac{1}{8}$ inch.

The 4400-volt transformer is connected to the arc through a ballast resistance of about 2800 ohms which fixes the arc current at 1.5 amperes. The resistance is built up of individual units of about 300 ohms, each wound of No. 24 Copel wire on transite cards. The units are mounted on edge in a protecting cage, and the normal air circulation gives adequate cooling.

A general view of the light source is shown in Fig. 4. The ballast resistance is seen behind the

arc stand. The arc stand is provided with a protective housing, shown open. This housing must be closed, actuating push switches in the primary circuit, before the transformer current can be turned on.

A Bausch and Lomb quartz spectrograph of the Littrow type is used. The region covered on the plate from 3600A-2800A, contains suitable lines for the analysis of each element handled. The light source is about 25 cm from the slit. It is imaged on the spectrograph optics by a lens placed just in front of the slit. This imaging insures a uniform distribution of light along the spectrum line, since each point of the source contributes light to each point of the slit and of the spectral line image, and, further, each part of the illuminated portion of optics contributes light to each point of the line image.

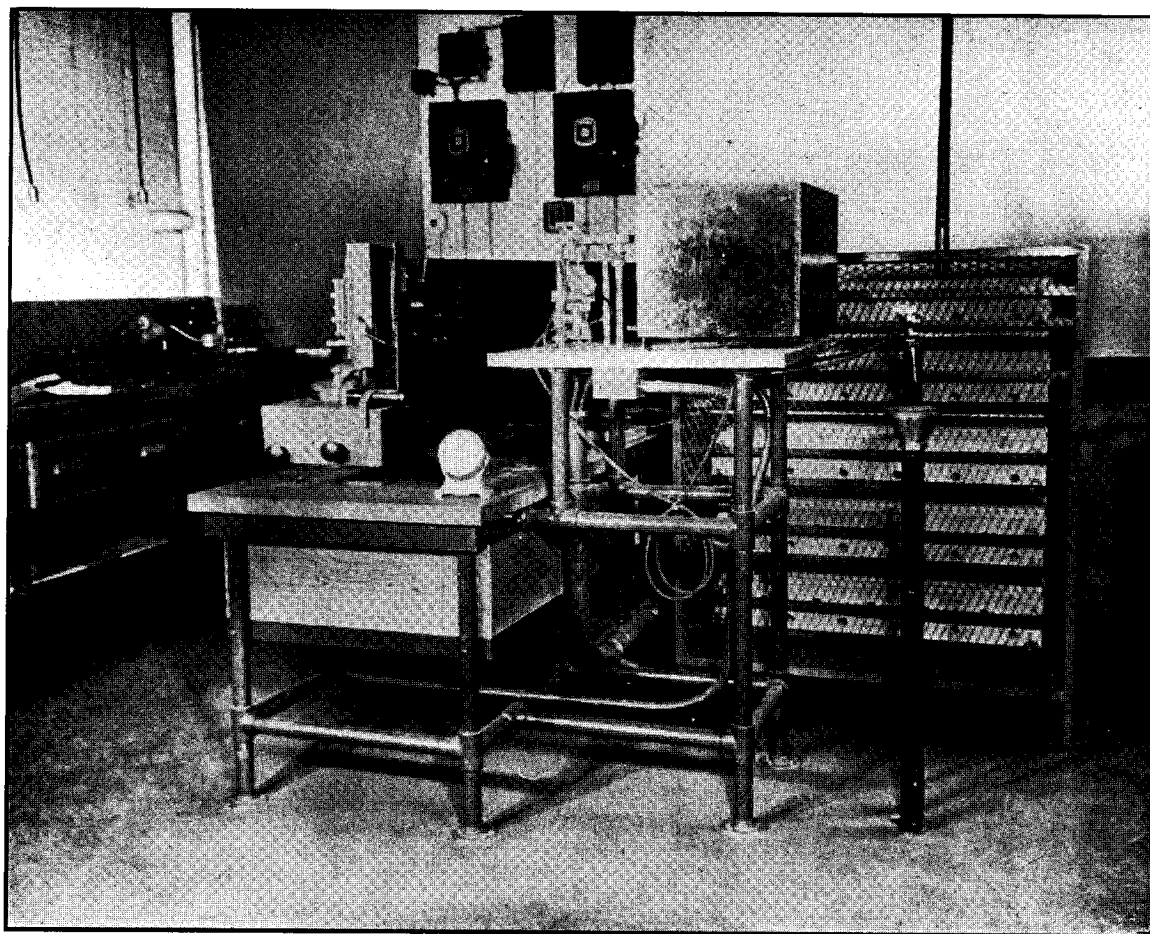


FIG. 4. View of source and spectrograph.

The spectrograph and light source are in the same room, a convenient arrangement for a single operator. If a large volume of work is to be handled by two or more analysts, it is better to place the spectrograph in the dark room with one operator and to place the light source in an adjoining room to be tended by a second operator.^{1,2} In the present installation a small adjoining dark room is used. It is equipped with the rocking trays and infra-red dryer described elsewhere⁶ for rapid plate processing. A third room contains the microphotometer, a Bausch & Lomb density comparator which has been remodeled as in the previously described installation. In the present work the microphotometer slit is set to cover 25μ of the spectral line width. The spectra taken with a 40μ spectrograph slit are nearly twice this width. Readings are taken by moving the spectral line image slowly across the microphotometer slit and observing the maximum galvanometer reading. Since the galvanometer has a period of 2 seconds a reading on a line may be made readily in 5 or 6 seconds.

Experimental Procedure

Two strips an inch wide by any convenient length, are cut from the sheet steel for analysis, and one strip is mounted in each of the water-cooled clamps. Following a pre-exposure burning of the arc for 30 seconds, the spectrograph shutter is opened and the analysis exposure made. The equipment is at present calibrated for the analysis of chromium, copper, nickel and tin in the ranges of approximately 0.01 percent to 0.10 percent. With the lines of these elements available in the spectrographic region, it is not possible to perform analyses of all four of these elements with one exposure. An exposure of 3 to 5 seconds has been found satisfactory for chromium and copper, twenty seconds for nickel and forty seconds for tin. A spectrographic slit length of 6 mm is used and twelve spectra can be recorded on a plate four inches wide. Thus the spectra for the analysis of all four elements in three samples can be placed on one plate. If a large number of samples were to be handled, time and plates could be saved by making the four exposures on one sample concurrently in one spectrum using three movable diaphragms to cover successively the plate regions of the analytical lines of copper,

chromium and nickel, as their exposures were completed, while the tin exposure continued the full forty seconds.

The processing of the photographic plate is carried out in a minimum of time with the help of the dark room accessories mentioned above. Since extreme speed is not required in the work, the most rapid developers are not used. However, processing can be completed in about six minutes. It has been found desirable, even if speed is not essential, to use rocking trays and rapid drying to insure uniform results.

The interpretation of the plates with the help of the microphotometer involves two steps. First, the plate calibration, or relation between plate blackening and exposure, is obtained, as in the cast iron analysis, by reading the galvanometer deflections on the microphotometer for several iron lines whose relative exposures have been determined previously for the equipment used. From these readings, a calibration curve of the plate emulsion is plotted showing the logarithm of the exposure as a function of galvanometer deflection. The relative exposures or intensities of any lines may be determined at once from this curve when their galvanometer deflections are known, since the difference of the logarithms of their exposures is the logarithm of the ratio of their exposures.

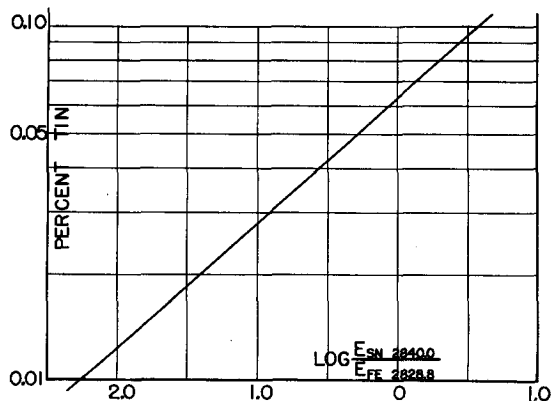


FIG. 5. Analytical curve for tin.

The next step is to determine from the microphotometer readings, by use of the calibration curve the logarithm of the ratio of the relative intensities of a selected line of each element under analysis and of a selected comparison iron line. For each element there has been drawn

previously an analytical curve showing, from measurements on chemically analyzed samples, the variation of this log *E* ratio with percentage concentration of the element in the sample. Fig. 5 shows such an analytical curve for tin. From this curve the concentration of the element in the sample is read.

The whole process of analysis on a single sample need not consume more than ten or twelve minutes including about two minutes for loading the sample and plate holder, and making the exposure, six minutes for processing the plate, and two or three minutes for the microphotometer readings and transposition to percentage content. Obviously, if several spectra are recorded on a single plate, and two operators are used, the rate at which analyses can be made may be greatly increased.

A major difficulty in the spectrographic analysis of metals at these low concentrations in steel is that of obtaining from chemical analysis satisfactory composition data upon which to base the analytical curves. Since the concentrations in this work are near the limit of sensitivity of the usual wet methods of analysis, it has been found desirable to average the results of several chemical determinations if possible by two or more laboratories. A check on the chemical results is given by the requirement that the analytical curve, plotted from measurements on a series of samples graded by chemical analysis, must be smooth. The curve may thus be better than the individual points, although the question will be left of a possible additive correction factor.

Accuracy and Reliability

In this range of composition an individual spectrographic analysis is more reliable than an

TABLE II.

LIFT	SAMPLE	Cu	Cr	Ni	Sn
693	1	0.071	0.01-	0.025	0.01-
	2	.085	.01-	.018	.011
	3	.082	.01-	.020	.01-
694	1	.086	.013	.022	.014
	2	.085	.01-	.017	.011
	3	.076	.01-	.018	.01-
691	1	.069	.01-	.017	.011
	2	.062	.01-	.017	.011
	3	.077	.01-	.022	.01-
692	1	.073	.01-	.020	.01-
	2	.075	.01-	.023	.01-
	3	.072	.01-	.010	.01-
695	1	.098	.01-	.018	.01-
	2	.10+	.01-	.016	.013
	3	.072	.01-	.018	.010
696	1	.064	.01-	.017	.010
	2	.084	.01-	.018	.011
	3	.059	.010	.018	.012
697	1	.060	.01-	.019	.01-
	2	.062	.01-	.017	.011
	3	.075	.01-	.016	.01-
698	1	.093	.010	.018	.01-
	2	.063	.010	.018	.01-
	3	.063	.010	.023	.01-

individual chemical analysis so that chemical checks of spectrographic results are of little value. Estimates of the reliability of the analyses can be obtained by comparison of repeated measurements on the same sample.

Table I gives the results of two typical tests in the University laboratory made to determine how closely determinations on nickel and chromium could be repeated. In each case the individual determinations were made on separate spectra from the same sample recorded on the same photographic plate. The percentage deviation from the mean, and the squared percentage deviation are given; the standard deviation ($\Sigma d^2/(n-1)$)^{1/2} is computed. The standard deviation, sometimes called the mean error of a single observation, should be exceeded in only 31.7 percent of the cases in a series of measurements; and three times this deviation should occur only once in 375 cases. Extensive tests of the equipment and method have shown that at concentrations found in this work standard deviations of from 3 to 6 percent are to be expected. Since the present ranges of analysis are for chromium

TABLE I.

% Ni	Dev. %	(Dev. %) ²	% Cr	Dev. %	(Dev. %) ²
0.0315	5.04	25.4	0.0438	2.65	7.0
0.0305	1.70	2.9	0.0489	8.69	75.5
0.0306	2.03	4.1	0.0414	7.98	63.7
0.0291	2.97	8.8	0.0421	6.43	41.4
0.0287	4.30	18.5	0.0465	3.35	11.2
0.0302	0.70	0.5	0.0463	2.91	8.5
0.0295	1.64	2.7	0.0443	1.48	2.2
0.0298	0.64	0.4	0.0460	2.24	5.0
			0.0455	1.13	1.3
Mean 0.02990	Σd^2 63.3		Mean 0.04499	Σd^2 215.8	
Standard dev. = $(\Sigma d^2/(n-1))^{1/2}$ = 3.0%			Standard dev. = $(\Sigma d^2/(n-1))^{1/2}$ = 5.2%		

0.02–0.10 percent, for copper 0.01–0.04 percent, for nickel 0.01–0.10 percent, and for tin 0.01–0.10 percent, this accuracy represents determination to 0.01 percent or better in concentration.

In the plant laboratory repeated measurements are not ordinarily taken on the same sample. Some data are available of measurements on samples cut from different parts of a strip rolled from the same lift, or part of a billet. Variations between these measurements may be due to the method or to real variations in the sample, or both. The general close agreement is an indication of the uniformity of the product and of the accuracy of the analytical procedure.

Table II shows some typical data from the spectrographic laboratory of the Great Lakes Steel Company. Results from a number of lifts are shown, and for each lift three different

samples were tested from widely spaced portions of the resulting strip. The results are given in percent. 0.01-indicates less than 0.01 percent, an amount considered to be of no importance.

It will be seen that the spectrographic method permits determinations of metallic constituents of steel as low as 0.01 percent to be determined to 0.001 percent or 0.002 percent, or with an accuracy of about 10 percent. The sensitivity and accuracy are adequate for the present problem. The speed is much better than that of chemical analysis and the technique is of a simple routine nature.

It is a pleasure to express our appreciation to Mr. L. Selmi and Mr. C. L. Altenburger of the Metallurgical Department of the Great Lakes Steel Company for their assistance and cooperation.

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6. H. B. Vincent and R. A. Sawyer, *Spectrochimica Acta* **1**, 131 (1939).

Calendar of Meetings

July

24–26 American Society of Civil Engineers, Denver, Colorado

August

27–30 American Institute of Electrical Engineers, Los Angeles, California

September

9–13 American Chemical Society, Detroit, Michigan

October

2–4 Optical Society of America, Rochester, New York
7–11 National Safety Council, Chicago, Illinois
18–19 Society of Rheology, New York, New York
21–26 American Welding Society, Cleveland, Ohio
21–25 American Society for Metals, Cleveland, Ohio
28–30 National Academy of Sciences, Philadelphia, Pennsylvania
28–Nov. 2 Conference on Applied Nuclear Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts