TABLE III. ANALYSES OF IODINE SOLUTIONS BY SODIUM THIO-
SULFATE AND BY ARSENIOUS OXIDE

Na₂S₂O₃ Sample No.	Normality by Na₂S₂O₃	Normality by As₂O₃	Normality Calcd. from I₂ Content
1 recrystallized	0.04256	0.04253	0.04255
2 recrystallized	0.04323	0.04319	0.04320
3 recrystallized	0.04254	0.04253	0.04255
4 recrystallized	0.04322	0.04319	0.04320

TABLE IV. ANALYSES OF CERIC SULFATE SOLUTIONS BY SODIUM
THIOSULFATE AFTER PROLONGED EXPOSURE TO LIGHT

Sample	Normality by Na₂S₂O₃	Normality by Mohr's Salt	Deviation %
1 recrystallized	0.04564	0.04562	0.04
2 recrystallized	0.04572	0.04562	0.22
3 recrystallized	0.04565	0.04562	0.07

for a month over calcium chloride. Further substantiation of this stability toward light, in the absence of moisture, is presented in Table IV. These samples were stored similarly for 11 months, then separate portions (0.25 to 0.35 gram) were titrated with ceric sulfate solution (2).

In order to determine the possibility of decomposition of anhydrous sodium thiosulfate exposed to both light and air, portions were exposed to the atmosphere of the laboratory in weighing bottles set in beakers covered with watch glasses. After known periods of exposure, the samples were heated at 120° C. to constant mass, and separate portions were titrated with the ceric sulfate previously employed.

Typical resulting data appear in Table V. Obviously, detectable decomposition had not occurred.

Finally, sodium thiosulfate was found to be not appreciably hygroscopic and readily redriable to constant mass. A portion of sample 5 which had taken on 1.6 per cent of its weight of water during 7 days' exposure to the air was dried to its original mass in 2 hours at 120°. A portion of sample 1 with similar surface exposed showed no change in mass over a period of 6 days under similar conditions. A 4.503-gram por-

tion of sample 2 gained 48 mg. in 18 days but was redried completely in 1 hour at 120°.

Summary

The stability of anhydrous sodium thiosulfate has been investigated. No decomposition has been indicated by the critical method of reaction velocity measurements with sodium bromoacetate when the salt was kept at 120° C. for 79 days. The dehydration of sodium thiosulfate pentahydrate produces an anhydrous salt which fulfills the requirements of a primary standard.

TABLE V. EFFECT OF EXPOSURE TO LIGHT AND AIR UPON COM-
POSITION OF SODIUM THIOSULFATE

(Normality of Ce(SO₄)₂ by Mohr's salt, 0.04562)

Sample	Days Exposed	Normality of Ce(SO₄)₂ by Na₂S₂O₃	Deviation %
1 recrystallized	18	0.04561	0.02
	24	0.04563	0.02
	32	0.04557	0.11
2 recrystallized	19	0.04559	0.07
	31	0.04562	0.00
3 recrystallized	21	0.04560	0.04
	34	0.04564	0.04
5 recrystallized	0	0.04557	0.11
	23	0.04562	0.00

Literature Cited

(1) Chapin, J. Am. Chem. Soc., 41, 351 (1919).
(2) Furman and Wallace, Ibid., 53, 1283 (1931).
(3) Kamner, dissertation, Columbia University, 1934.
(4) La Mer, J. Am. Chem. Soc., 51, 3341 (1929).
(5) La Mer and Fessenden, Ibid., 54, 2351 (1932).
(6) La Mer and Kamner, Ibid., 57, 2662, 2669 (1935).
(7) La Mer and Tomlinson, IND. ENG. CHEM., Anal. Ed., 9, 588 (1937).
(8) Slator, J. Chem. Soc., 87, 481 (1905).
(9) Tomlinson, dissertation, Columbia University, 1939.
(10) Young, J. Am. Chem. Soc., 26, 1028 (1904).

Quantitative Spectrochemical Method
for Zinc Die Casting Analysis

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THE literature of the last few years pertaining to spectrochemical analysis by means of the emission spectrum indicates clearly that a new era in speed, accuracy, and dependability of this type of analysis has been ushered in. The 10-minute analysis of steel for silicon, manganese, chromium, nickel, and molybdenum, with an inaccuracy of less than 3 per cent of the quantity being measured in all cases, is a typical example (4, 5, 6). These gains in speed, accuracy, and dependability have been achieved through no revolutionary innovations but rather through a realization of all the factors making for a good analysis. Apparatus designed with these factors in mind is now available, so that any laboratory can be assured of definite results in connection with the analysis of certain materials.

The extension of these contemporary methods to the analysis of a wide variety of materials is the immediate need in spectrochemistry. The development of a new modification of the standard direct current arc (1) by these laboratories has made possible rapid and accurate analyses of materials that have been analyzed heretofore by tedious spectrographic or chemical methods. The present paper describes the ap-

plication of this source and a standard group of instruments to the analysis of one such type of material, zinc die casting alloys.

Since 1935 the American Society for Testing Materials has recommended a spectrochemical method (2) suitable for the analysis of lead, tin, cadmium, magnesium, iron, and copper in both zinc and zinc alloys such as are used in die casting. The method has enjoyed considerable popularity due to its inherent advantages when compared with routine chemical methods.

These advantages are, in the main, connected with the spectrograph's ability to register lines of the various elements just as accurately at very low concentrational levels as at the higher levels. In other words, the spectrograph allows a constant degree of accuracy nearly independent of the quantity of an element present. For this reason errors in this analytical method are always referred to as a certain percentage of the quantity present, be that quantity 0.001 or 10 per cent. Many routine chemical methods, on the other hand, have a fixed absolute error expressed as a certain percentage of the entire sample and not dependent upon the amount being

measured. When this amount approaches the absolute error, very large variations in answers will be obtained by different analysts and even the most accurate methods fail.

In producing die castings it is imperative that lead, tin, and cadmium be determined down to concentrations of 0.001 per cent, as little more than this can be tolerated in the better castings, and other constituents like magnesium, iron, and copper must often be held to lower levels of a few hundredths per cent. Thus, by and large the problem appears ill suited for analytical chemistry and rather ideally suited for spectrochemistry. Experience has borne out this conclusion time and again, always giving impetus to the greater use of spectrochemical methods.

Of the various spectrochemical methods available, the A. S. T. M. method has a simplicity and straightforwardness that has made it the model for many analyses of this type. In general, however, the method does not lend itself to the latest trends in spectrochemistry: (1) to eliminate the use of standards except for the original calibration and occasional check of the analytical system; (2) to eliminate all complicated sample preparation; and (3) to increase the accuracy of analyses over those previously available. The method described here, on the other hand, lends itself admirably to the very latest practices, thus ensuring speed, certainty, and a high degree of accuracy. Two ways of handling the original samples are described.

Metal Peg Analysis

To achieve 2 man-minute analyses sample preparation must be reduced to a minimum. Working with the metal directly is the most rapid. In foundry work where the molten metal is available, sample rods may be cast to the required dimensions. In testing fabricated stock, small rods can usually be machined in a very short time. The test rods utilized are 0.23 cm. (0.094 inch) in diameter and 2.2 cm. (0.875 inch) long, and fit directly into a special base illustrated in Figure 1. This base also holds an insulating Transite bushing, over which is placed a graphite sleeve. Ammonium chloride is used to fill the space between the rod and the sleeve. The analytical reagent grade, produced in a finely powdered form, works very well without any grinding or preparation, except that it must be well dried before using. In practice it is kept in a desiccator over sulfuric acid. The Transite bushings and the graphite sleeves may both be used over and over again, the former being cleaned mechanically, the latter by nitric acid treatment.

The arc is completed with the upper electrode shown, produced by pushing a small length of 0.3-cm. (0.125-inch) carbon electrode into a 0.6-cm. (0.25-inch) carbon, drilled and slotted to receive the smaller size. The arc is operated with the electrodes 0.9 cm. (0.375 inch) apart and must be exactly aligned with the spectrograph. The arc-spark stand utilized allows the projection of images of the electrodes onto a marked ground-glass screen which provides exact spacing and alignment. The arc is struck by lowering the top electrode with a knob mechanism, and is then spaced by turning this knob until a stop is reached. Because of the very short arcing times employed, 4 seconds, it is necessary that the arc may be accurately spaced in a few tenths of a second. The 4-second interval is controlled by an electric timer on the rectifier which extinguishes the arc after operating the preset time. Ten amperes are passed through the arc circuit, this value being attained just as the arc is opened to its full spacing. To insure reproducibility of this value the standard rectifier is adjusted before arcing to supply 14 amperes when carbon electrodes are short-circuited in the arc-spark stand.

This type of arc blows a large volume of sample through the discharge by means of the gas formed by decomposing ammonium chloride, and because of this action has been termed a "high streaming velocity arc". In the 4 seconds of arcing about 75 mg. of sample are forced up through the discharge. This makes for high atomic concentrations and great spectral intensity, so that a single 4-second exposure is adequate to produce an intense photographed spectrum with the high-resolution grating spectrograph employed.

This same type of arc has been tested on a variety of metals and found to give very promising results. An iron peg of the

same dimensions as the sample peg gives a highly reproducible arc when operated with ammonium chloride and 7.5 amperes in the arc circuit. For this value the rectifier is adjusted to 10.6 amperes on short circuit. Lengths of finishing nails of the correct diameter furnish the iron rods, which are held in the same type of holder as the sample rods. Extended tests have shown that the relative intensities of the various iron lines as produced in this arc are reproducible to a few per cent, which is much better than was obtainable with any other iron arc tried, including that reported by Slavin (3).
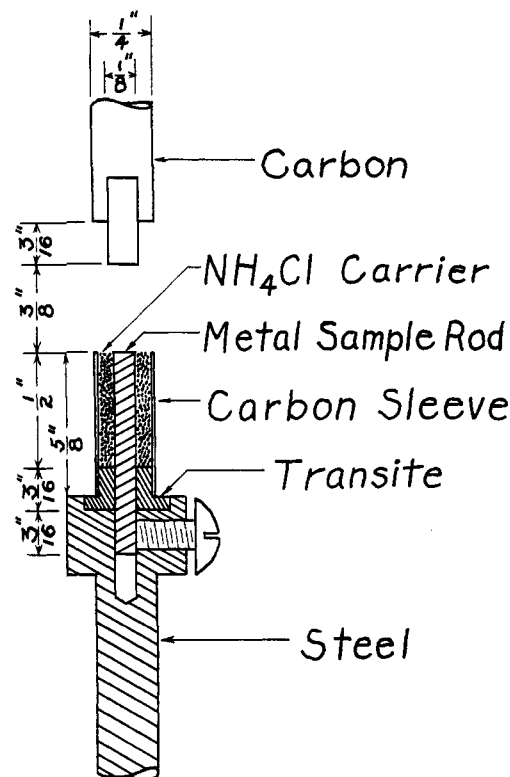

FIGURE 1

The constancy of the relative intensities in this arc makes it entirely suitable for film calibration, as to both emulsion contrast and sensitivity in the various regions of the spectrum. At the same time it is used for line identification in connection with a standard dual projection comparator. Thus two sources are available, one for sample analysis and one for film calibration.

The spectrograph used to photograph the spectra is a standard A. R. L. grating spectrograph with good dispersion and resolution. Its dispersion, 7 Å. per mm., is adequate to give good line separations with the 60-micron slit used for accurate densitometry even with considerable iron in the samples. This also allows accurate measurement of background next to the line, which is very important when making quantitative determinations close to the limit of detection. Another point in connection with background measurements is that not much scattered light can be tolerated in the spectrograph. The superiority of the concave grating spectrograph over a prism instrument in this respect is really worth while whenever very small concentrations must be measured with high accuracy. The standard ultraviolet range of the spectrograph, 2380 to 4600 Å., was used for all the quantitative determinations involved in zinc die casting material analysis. However, a special range, 2280 to 4500 Å., which includes the 2288 cadmium line and all other lines needed, was also available and could be used regularly just as well as the standard range if higher sensitivity for cadmium analysis were essential.

The optical system between the spectrograph and the source is simple and convenient. A rotating sector and aperture, placed at the secondary source plane of the astigmatic grating spectrograph, controls the speed of the instrument and defines the spec-

TABLE I. TYPICAL ANALYTICAL DATA

Iron Calibration Spectrum

Calibration group

1. Wave length, Å.	2788.1	2786.8	2786.2	2781.8	2778.8	2778.2	2767.5			
Known relative intensity	1.92	0.219	0.126	0.619	0.519	1.18	1.00			
Percentage transmission[a]	8.8	72	88	35.7	42.0	15.1	19.5			
2. Wave length, Å.	3173.7	3172.1	3171.4	3168.9	3166.4	3165.9	3164.3	3163.9	3163.1	
Known relative intensity	0.97	0.64	1.00	0.65	1.95	1.32	0.35	0.42	0.22	
Percentage transmission	37.4	52.3	35.7	52.0	18.0	27.1	75	68.8	88	
3. Wave length, Å.	3953.8	3948.8	3948.1	3947.5	3947.0	3943.4	3942.4	3940.9	3940.0	3852.4
Known relative intensity	0.136	1.20	0.86	0.57	0.44	0.24	0.77	0.80	0.066	1.00
Percentage transmission	65.0	6.8	10.3	16.8	23.0	43.0	11.8	11.2	87	8.6

Die Casting Alloy Spectrum Example

Element	Zinc	Magnesium	Copper	Aluminum	Tin	Cadium	Iron	Lead
Wave length of line, Å.	2670	2783	2961	3064	3175	3261	3737	4058
Transmission of line and background	11.2	14.7	13.3	24.1	89	61.2	16.6	80.3
Transmission of background	90	66	84	78	95	89	99	99
Calibration group used	1	1	1	2	2	2	3	3
Intensity of line and background	1.57	1.24	1.36	1.48	0.21	0.52	0.58	0.087
Intensity of background	0.11	0.25	0.15	0.32	0.15	0.21	0.029	0.029
Intensity of line	1.46	0.99	1.21	1.16	0.06	0.31	0.55	0.058
Intensity ratio to Zn line	...	0.68	0.83	0.79	0.04	0.21	0.38	0.040
Multiplicative constant, α	...	0.052	1.38	4.78	0.0252	0.0131	0.0608	0.069
% of element present	...	0.035	1.14	3.77	0.001	0.0027	0.023	0.0028

[a] Percentage transmission is referred to clear film transmission, which is considered as 100%.

tra vertically. This same sector carries on its periphery a stepped sector which may be used for density calibration if desired. The source is 25 cm. beyond this aperture, no lenses being employed between it and the spectrograph unless the stepped sector is used.

The camera of the spectrograph takes a 3000-cm. (100-foot) roll of 35-mm. motion picture film. A 31.6-cm. (12.625-inch) length is used to photograph spectra of eight samples and one standard iron. This length is removed through an aperture at the side of the camera. The spectrograph is then ready for the next set of analyses. Eastman Par Speed film is used to ensure approximate equality of contrast throughout the spectral range photographed. An Inconel film holder and a developing machine allow convenient film processing. To ensure uniform development over each portion of the film a modified brush development technique is used, employing a rubber blade on a paddle which is moved along the length of the film about 0.16 cm. (0.06 inch) above the emulsion. This is spaced from the film accurately by the handle of the film holder.

The D-72 stock developer used provides adequate development in approximately 1 minute. A few seconds in the short stop arrests development. Fixing is achieved in 1 minute, washing in 0.5 minute, and drying takes another 3 minutes. Thus, the total film processing time is about 6 minutes.

The film, when dried, is placed in a standard dual projection comparator. By alignment between the iron spectrum on the film and one on the master, the wave length of any line in the spectrum can be read directly from a scale on the master. Besides this, most of the lines used in the analysis are shown and labeled on the master plate directly, so that line identification is very rapid and certain. Transmission readings on these lines are obtained with a standard photoelectric densitometer. By utilizing a mechanical sweep on the densitometer and slit mechanism, this instrument allows readings accurate to a few tenths of a per cent to be made very rapidly. The actual readings used are on the lines shown in Table I.

The relative intensities of each group of iron lines were determined by standard stepped-sector methods. Once these were obtained, however, they were used for film calibration at all times. Successive lines appearing in the iron spectrum in one region of the spectrum make a calibrating set for that region. By arbitrarily calling one line unit intensity, all readings taken in that region can be converted to intensities with respect to this unity line. This can be done in each region of the spectrum separately, irrespective of the changing film contrast or sensitivity from one region to the other. Comparison between intensities of lines in different regions can also be made, since the unity lines in the different regions of the spectrum maintain their relative intensities constant with this type of iron arc. Thus, instead of measuring, for instance, $\frac{I(\text{Pb4058})}{I(\text{Zn2670})}$ directly, which is impossible photographically because of the indeterminate film sensitivities in the two regions, $\frac{I(\text{Pb4058})}{I(\text{Fe3852})} \frac{I(\text{Fe2767})}{I(\text{Zn2670})}$ is measured, which is possible

photographically. Since $I(\text{Fe2767})/I(\text{Fe3852})$ is a constant it can be absorbed into the other calibrating constants of the system. Thus, this method of calibration allows the intensity comparison of any two lines appearing in the photographed spectrum, irrespective of their difference in wave length. This allows the use of a single zinc line 2670 as an internal standard for all element lines, irrespective of the region of the spectrum in which they appear.

It may be seen from Table I that the spectrum has been divided into three regions, each being calibrated and used for certain determinations. The actual conversion of line transmission readings to intensity values is done on a calculator.

The principle of operation is simple. A plot of the data using log transmission as ordinates and log intensities as abscissas gives three film calibration curves. The first group of lines of the alloy spectrum would be read from curve one, the 2800 Å. region calibration, the second from curve 2, etc., giving the intensities. Besides the intensity of the line, which really represents line plus background, the background intensity can be determined from a transmission reading next to the line. Then by subtracting this intensity value from that of the line plus background, a true line intensity is obtained. This is illustrated in the example.

It is obvious from the size of this correction that it cannot be ignored. In fact, it is only by making such a correction that accurate results can be obtained at very small concentrations when a line superimposed on the background may have only a fraction of the background intensity. From these corrected intensities the ratios of intensities are determined with reference to the internal standard zinc line. The ratios for lines in groups 2 and 3 have an arbitrary factor included in this ratio, but since this is a constant it introduces no complications into the system.

With the intensity ratios available the final conversion to percentage can be made. This requires that these ratios be obtained from runs on a number of samples of known composition, so that the relationship between intensity ratio and percentage may be established. A method of obtaining accurate analyses of standards is given below. For all the elements in question, over a certain range of percentages, a direct proportionality exists between intensity ratio and percentage $C = \alpha I$ (element line)$/I$(standard line). Thus, by determining α for each element the complete analytical system is determined. These constants are given in Table II, together with the range of percentages in which they can be used. From them the percentages of the example shown in Table I were obtained. The fact that a single constant can be used to define the analysis of each element is very convenient and represents one of the main advantages of this type of source when coupled with this manner of calculation.

This procedure may appear involved, but it serves for the calculation of the analyses of eight samples for seven elements each or fifty-six individual element analyses. A special calculator including various rules, which allows the final percentages to be obtained directly from the transmission values, was used in the actual tests and calibration of the system. This calculator will be described in detail at a later date.

For lead, tin, and cadmium the lower percentage figure of Table II represents the lowest limit that can be measured with an accuracy of 0.0001 per cent. All the other limits can be extended to lower or higher percentages as required. The accuracy obtainable in the analysis of the various elements has been studied in some detail. When eight pegs cut from a pig are used to obtain eight repeat analyses, assuming that no segregation exists, the inherent errors of the spectrographic method are easily calculated. This has been done for each element and at a number of different concentrations when samples were available. The results have been very gratifying, indicating a new degree of accuracy in arc-spectrum analysis. Aluminum at 4 per cent can be analyzed with an average error of 0.1 per cent, if good nonoxidized metal pegs are available. Copper determinations show an average error of 2 to 3 per cent of the quantity being measured, or about 0.03 per cent at 1 per cent and 0.09 per cent at 3 per cent. Magnesium and iron values have an average error of from 4 to 6 per cent of the quantity being measured, 0.0006 per cent at 0.01 per cent and 0.004 per cent at 0.1 per cent. The accuracy of determinations at the lower limit of detection of lead, tin, and cadmium has been indicated above, while the average error at 0.01 per cent is approximately 5 per cent of that quantity or 0.0005 per cent.

A set of eight analyses requires 18 minutes to set up and arc the sample pegs, 6 minutes to process the film, 30 minutes to obtain the transmission readings, and 30 minutes' calculating time, or a total of 84 minutes to obtain 56 individual analyses. This represents an average time of less than 2 man-minutes an analysis if sample rods are available.

Thus, a metal rod analytical system has been devised for die casting alloys which is comparable in speed and facility to the spark method of iron analysis. The fact that it furnishes accurate analyses in both the 1 to 4 per cent range and the 0.001 to 0.01 per cent simultaneously shows that the source used is a valuable addition to the present types of spectral sources available.

TABLE II. CALIBRATING DATA FOR METAL PEG ANALYSIS

(Using 2670 zinc line as an internal standard)

Element	Wave Length of Line Å.	Range Covered %	Multiplicative Factor, α	Calibration Group
Magnesium	2783	0.01-0.1	0.052	1
Copper	2961	0.05-1.0	1.38	1
Aluminum	3064	3.5-4.5	4.78	2
Tin	3175	0.0009-0.01	0.0252	2
Copper	3194	0.3-3.0	3.00	2
Cadmium	3261	0.0009-0.01	0.0131	2
Iron	3737	0.01-0.1	0.0608	3
Lead	4058	0.0006-0.01	0.069	3

Metal Oxide Analysis

There are certain cases where it is either not possible or advantageous to obtain a rod for analysis. In the case of custom work, drillings are often submitted for analysis, while when large samples must be tested, drillings from various portions are necessary to furnish a truly representative sample. In that case acid solution must be used to furnish the smaller representative sample used in an arcing. It was to work with this type of sample that the A. S. T. M. (2) method was devised.

It is much more important to have a nonmetallic sample method available for analysis of the standards used to calibrate the metal peg arcing method. These could be analyzed by another method—for instance, chemical analysis—but any errors inherent in that analysis would be reflected in the final system. However, with the nonmetallic sample method available any metal sample can be reduced to a nonmetallic and compared directly with synthetically prepared nonmetallics produced by the addition of known amounts of all the constituents. Once the analysis of certain samples is thus determined, metal pegs of this material can serve as standards for the direct metal peg analysis.
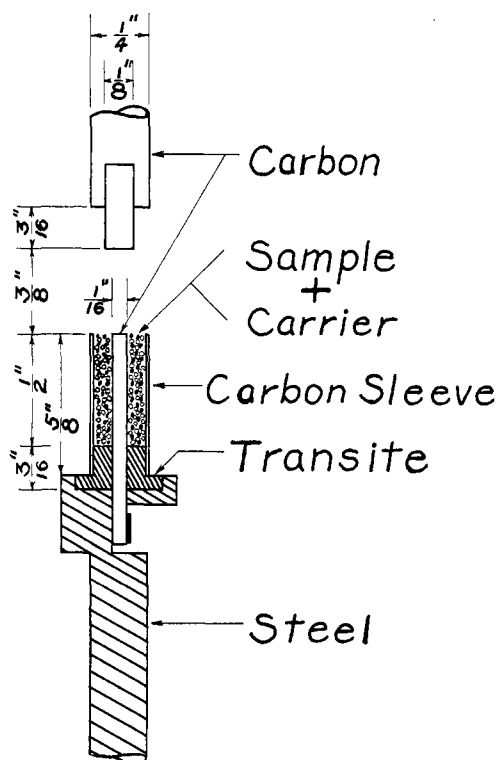

FIGURE 2

The method devised utilizes powdered oxides prepared from solution of the sample in acid. The procedure given below was devised after many tests and represents the one that gave the most reproducible results day after day. It has been checked for possible loss of any constituents and found satisfactory in this respect. It should be followed closely to assure the production of oxides in a manner that can be reproduced from sample to sample and from time to time.

A mixture of 5 cc. of water, 5 cc. of concentrated nitric acid, and 0.5 cc. of concentrated hydrochloric acid per gram of metal is used to dissolve the sample. Water and acid are mixed in the order given just before adding them to the metal. The sample plus acid is heated until all the metal appears to be in solution and then let stand hot for 5 minutes. The final oxides are formed by pipetting this solution drop by drop into a silica dish with a flat bottom, heated to about 350° C. Drops should be placed all over the bottom of the dish, each one forming oxides in turn. This allows each drop to go through the liquid, solid nitrate, solid oxide transition as an individual portion. Only by such treatment is it possible to secure oxides that give reproducible results no matter when produced. Larger volumes of solutions heated to produce oxides gave erratic results, probably because of the possibility of forming a variety of compounds of zinc, aluminum, and oxygen, depending upon the exact heating cycle.

An analogous effect probably occurs when electrodes are prepared with 0.1 cc. of acid solution of the sample in the A. S. T. M. method, as it is impossible to duplicate intensity ratios from day to day with that method. It is probably for this reason that

TABLE III. CALIBRATING DATA FOR OXIDE ANALYSIS

(Using 2670 zinc line as an internal standard)

Element	Wave Length of Line Å.	Range Covered %	Multiplicative Factor, α	Calibration Group
Magnesium	2783	0.01-0.1	0.088	1
Iron	2813	0.01-0.05	0.11	1
Copper	2961	0.05-0.3	0.286	1
Aluminum	3064	3.5-4.5	4.12	2
Tin	3175	0.0002-0.01	0.0028	2
Copper	3194	0.3-3.0	0.76	2
Cadmium	3261	0.0007-0.01	0.0082	2
Lead	3683	0.0003-0.01	0.0091	3
Iron	4271.7	0.01-0.1	0.052	3

standards must always be prepared simultaneously with samples, so that they will all pass through the same heating and drying cycle. Accurate analyses can, of course, thus be attained, though at the price of always repeating the preparation of standards for each new batch of samples.

After an oxide has been prepared in the silica dish, it is removed by gentle scraping and ground in an agate mortar. It is then mixed with carbon as a carrier which is used to blow the oxide up through the arc. Sucrose that has been carbonized and ground in an agate mortar to <200-mesh produces carbon that reacts readily with the atmosphere to produce large volumes of carbon monoxide and carbon dioxide. A one to one mixture by weight of sample and carrier is used. Ammonium chloride could not be used, since it reacted with the zinc to form a compound of low melting point.

The carbon mixture is arced in an electrode such as is depicted in Figure 2. A 0.16-cm. (0.06-inch) carbon rod at the center carries the current, while a 0.6-cm. (0.25-inch) carbon sleeve 1.6 cm. (0.625-inch) long, insulated from the electrode with a Transite bushing, acts as the sample-holding chamber. To protect the Transite bushing from the intense heat produced, a layer of carbon is placed over it. Electrode carbon filings thermally insulate and yet do not tend to act as a carrier. The remainder of the space is filled with the reactive carbon-sample mixture, about 250 mg. being required. Light tapping allows complete filling.

The same spacing and alignment of electrodes as employed with the metal pegs are used. The current and timing are also the same. In preparing the set of standard oxides from which the metal oxide working curves were determined once and for all, standard solutions were used for most of the elements. These were neutral solutions of aluminum nitrate, 40 mg. of aluminum per cc.; magnesium nitrate, 1 mg. of magnesium per cc.; ferric nitrate, 1 mg. of iron per cc.; lead nitrate, 0.1 mg. of lead per cc.; cadmium nitrate, 0.1 mg. of cadmium per cc.; and a tin tartrate solution 0.1 mg. of tin per cc. in 0.2 N hydrochloric acid. The tin solution should be prepared just before using.

Take zinc metal of high purity and place 930 mg. in a dish. Then add 1 cc. of aluminum nitrate, 40 mg. of aluminum per cc. to the zinc, and 30 mg. of pure copper wire. Prepare a solution of each of the other solutions, 0.8 cc. in this case, and make up to 4 cc. with water when necessary. Add 5 cc. of nitric acid and 0.5 cc. of hydrochloric acid to this solution. Pour this over the prepared zinc, aluminum, and copper. Proceed just as in the case of a whole metal sample once the zinc has dissolved. This makes a standard oxide with 4 per cent aluminum, 3 per cent copper, 0.08 per cent magnesium and iron, and 0.008 per cent cadmium, lead, and tin.

Prepare two other standards of 1 and 2 per cent copper, 0.02 and 0.04 per cent magnesium and iron, 0.002 and 0.004 per cent cadmium, lead, and tin, but with 4 per cent aluminum in each case.

Careful tests showed that varying percentages of all test elements with the exception of aluminum had no effect on the analysis of each other. Varying percentages of aluminum do have an effect, but fortunately this element is controlled accurately in commercial alloys. Variations from 3.5 to 4.5 per cent did not affect the analyses of the other elements appreciably but did provide a linear change with percentage in aluminum line intensities as referred to zinc, that made possible the analysis of this element over this 1 per cent range.

Because of the effect of aluminum, separate standards must be prepared for alloys without aluminum. A detailed presentation of this effect will be given elsewhere.

All the other spectrographic procedure is exactly the same as for the metal pegs, except that some other spectrum lines are used and where the same line is used a different intensity is obtained, owing to the different chemical form of the sample. For

convenience these data are presented in Table III. Again, just as in the metal peg case, simple multiplicative factors may be used to convert intensity ratios to percentage.

With such a method of sample oxide analysis available, calibration can proceed with the regular peg analysis. Duplicate sample pegs can be cut from the material to be analyzed, as indicated in Figure 3. Ends A are used for the metal peg arcing to
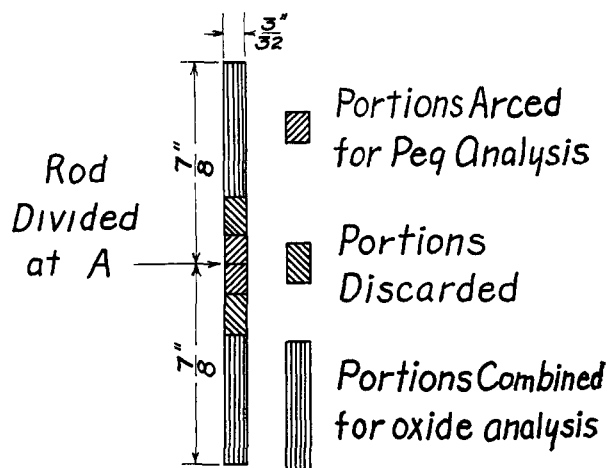

FIGURE 3

produce duplicate spectrograms. The oxidized portions are sawed off and the rest of the two pegs, about 1 gram, is combined and put into solution as indicated above. The oxide is then formed and analyzed by the powder procedure. This analysis, together with the intensity ratios obtained from the direct peg arcing, enables the multiplicative factors for the peg method to be deduced. After these factors have been checked a few times on a variety of samples covering the analytical working range, the system may be considered as calibrated. The factors so obtained should be similar to those given in Table II, as this system of calibration is such that differences in equipment should cancel out to a considerable extent. However, such calibration is essential if the full accuracy of the system is to be realized.

Summary

A complete spectrochemical system has been devised for the analysis of zinc die casting material. A method of calibration is presented, as well as all the analytical factors obtained by the authors. This should allow immediate use of the system by any laboratory equipped with a direct current arc source, a spectrograph of adequate dispersion, and a precision densitometer. The arcing methods described can, of course, be used without a densitometer but with standards to form a modified A. S. T. M. method.

Acknowledgment

Literature Cited

(1) Hasler, M. F., J. Optical Soc. Am., 31, 140-5 (1941).
(2) Nitchie, C. C., IND. ENG. CHEM., Anal. Ed., 1, 1-7 (1929).
(3) Slavin, Morris, Ibid., 12, 131-3 (1940).
(4) Vincent, H. B., and Sawyer, R. A., J. Applied Phys., 8, 163-73 (1937).
(5) Vincent, H. B., and Sawyer, R. A., "Proceedings of Seventh Summer Conference on Spectroscopy and Its Applications", pp. 16-19, New York, John Wiley & Sons, 1940.
(6) Zabel, G. W., and Schuch, John, Iron Age, 145, No. 18, 31-7 (May 2, 1940).