Table 111

Element	Recovery, %
Al	84.0
Ca	82.0
Čr	77.5
Fe	11.5
Ge	71.5
In	76.5
Mg	79.5
Pt	75.5
V	90.5
Zn	71.0
Av. (Fe omitte	ed) 78.7

Demonstrate Recoveries of Impunities on

sparked and the developed spectrum plate was photometered. Recoveries of impurities from the extraction were determined from the intensity ratios and the previously established working curves.

As expected, the recovery of iron was low because of the extraction of chloroferric acid by ether. The recoveries of the other elements were somewhat lower than would be expected from the distribution coefficients reported for them (1, 4, 9). Table III records the average per cent recoveries obtained for triplicate extractions of standard solutions. On the basis of these determinations it was shown that the gallium was at least 99.992% pure with respect to spectroscopically detectable elements.

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# Rapid Polarographic Method for Determination of Molybdenum in Iron and Steel

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HOLTJE and Geyer (3) observed that the wave height for the second step in the polarographic reduction of molybdate in perchloric acid is about ten times the wave heights obtained in other acid media (Figure 1). The nature of this effect and its possible application to the analysis of molybdenum-containing materials are under investigation in this laboratory. This paper shows that it is possible to use this effect for the rapid detection and determination of molybdenum in steel. Iron and steel samples containing 0.002 to 7.0% molybdenum and a large variety of





possible interferences have yielded good results by the procedure outlined below.

## NATURE OF POLAROGRAPHIC REDUCTION OF PERCHLORATE IN PRESENCE OF MOLYBDENUM

A kinetic study of the reduction of perchlorate chemically with stannous ion indicates that molybdenum(IV) is the active agent in bringing about the reduction (2). Reduction of molybdenum (VI) with zinc in perchloric acid does not proceed to molybdenum (III) until nearly all perchlorate is reduced to chloride. The great increase in current produced during the second step in the polarographic reduction of molybdenum(VI) in perchloric acid indicates that as soon as molybdenum(IV) is formed, perchlorate becomes reducible at the dropping mercury electrode. Molybdenum(III) does not give the effect. Chloride is a product of the reduction. Table I shows the effect of changing hydrogen ion concentration on the half-wave potential of the large wave. The wave height is unaffected by changes in hydrogen ion concentration as long as it is greater than 0.05 M. Table II shows the effect of changing molybdenum(VI) concentration on  $i_d$ . Table III shows the effect of changing perchlorate concentration on  $i_d$ .

At very low concentrations the diffusion current is nearly proportional to concentration of molybdenum(VI) or (V) in 1 M perchlorie acid, but it deviates increasingly from linearity above con-

Table I. Effect of pH Change  $[8.95 \times 10^{-5} M \text{ Mo}(VI), m^{2/3}t^{1/6} = 1.375 \text{ mg}, 2/3 \text{ sec}, -1/2]$ vs. S.C.E., Volt C1O<sub>4</sub> -M  $\frac{H}{M}$ id. ua.  $\begin{array}{c} 6.28 \\ 6.28 \\ 6.28 \\ 6.40 \end{array}$ . 00 . 00 . 00 . 00 . 168 . 206  $\begin{array}{c}
 0 \\
 5 \\
 1
 \end{array}$ 0.0 0.306 0.5 1.00 0.01 0.5101 4.891  $1 M H_2 SO_4$ 0.378 0.39

Table II. Effect of Molybdenum(VI) Concentration							
$(1 \ M \ HClO_4.m^{2/3}\ell^{1/6} = 1.375 \ mg.^{2/3} \ sec.^{-1/2})$							
$\operatorname{Mo}(VI),$ M	<i>id</i> , µа.	Mo(VI), M	id, μa.				
$\begin{array}{c} 8.95 \times 10^{-3} \\ 3.58 \times 10^{-3} \\ 8.95 \times 10^{-4} \\ 3.58 \times 10^{-4} \\ 8.95 \times 10^{-5} \end{array}$	143.5120.742.720.85.87	$3.58 \times 10^{-5}  8.95 \times 10^{-6}  3.58 \times 10^{-6} $	2.69 0.74 0.37				
Table III. Effect of Perchlorate Concentration							
$9.25 \times 10^{-4} M \operatorname{Mo}(VI)$ in 0.1 $M H^+$ (HCl + HClO <sub>4</sub> ). $m^{2/3}t^{1/6} = 1.375 \operatorname{mg}_{.2/3} \operatorname{sec}_{1/2}$							
$\begin{array}{c} \mathrm{HClO_{4,}}\\ M\end{array}$	$i_d$ , $\mu a$ .	id — μ8	0.51,				
$\begin{array}{c} 0.100 \\ 0.067 \\ 0.050 \\ 0.033 \\ 0.000 \end{array}$	2.52 1.97 1.65 1.22 0.51	2.0 1.4 1.1 0.7 0.0	)1 46 14 71 00				

centrations of 3 to  $10^{-5} M$ . Hydrogen ion is involved in the reaction. The increase over normal height expected for reduction of molybdenum(V) to molybdenum(III) is linear with perchlorate concentration at constant ion strength. Introduction of another substance such as sulfate decreases the wave height. Addition of 0.75 M sulfate to 1 M perchloric acid decreased the wave heights the same amount, regardless of whether sodium sulfate or sulfuric acid was used. The calibration curve used in analysis of steel is shown in Table IV.

Table IV. Calibration Curve

[Mo(VI) in 1.0 M HClO;]	and 0.75 M H <sub>2</sub> SO <sub>4</sub> ]	
Mo(VI),	id,	
M	μa	
$3.58 imes10^{-3}$	71.5	
$8.95 \times 10^{-4}$	25.8	
$5.37 \times 10^{-4}$	18.7	
$1.79 \times 10^{-4}$	9.33	
8.95 × 10 -	5.32	
$5.37 \times 10^{-3}$	3.26	
$3.58 \times 10^{-5}$	2.33	
1.79 X 10	1.09	

The wave height is dependent on the concentrations of molybdenum(VI) or (V) and perchlorate, although it is not a linear function of either. The presence of other salts or acid in the solution decreases the wave height. It has been found possible to polarograph molybdenum(VI) or (V) in acidic sulfate-perchlorate solutions in which the concentrations of these anions are carefully controlled and obtain consistent results regardless of what cations are present, so long as they do not give interfering waves, if hydrogen ion concentration exceeds 0.05 M. Oxidized forms of other elements whose reduced forms reduce perchlorate in solution do not give similar effects (1). Tungstic acid precipitates in solutions of the acidity in which studies were made. Acidified chlorate solutions behave like perchlorate solutions.

### APPLICATION OF EFFECT TO MOLYBDENUM IN IRON AND STEEL

As the molybdenum(V)-perchlorate polarographic wave height is at least ten times the height of a normal molybdenum(V) wave, and it occurs at an  $E_{1/2}$  much more positive than that for iron(II) to iron(0), it was felt that the molybdenum could be determined polarographically without prior removal of iron if the iron were kept in the ferrous state. Attempts to dissolve the samples directly in warm, dilute perchloric acid failed to yield good quantitative results, although molybdenum was detected in each case. It is not known whether incomplete solution or failure to oxidize molybdenum to the pentavalent state was responsible for low results obtained. Action of perchloric acid is extremely slow unless it is hot, and heating leads to oxidation of iron and reduction of perchlorate, both of which spoil the determination because ferric iron is reduced before molybdenum(V), and the concentration of perchlorate is critical.

Good results have been attained by dissolving samples in concentrated hydrochloric and nitric acids, converting the material to ferric sulfate, dissolving in sulfuric acid, reducing the iron with zinc amalgam, making the solution 1 M in perchloric acid, and polarographing. Wave heights are compared with a previously prepared calibration curve. Concentration of molybdenum(VI) or (V) was kept around  $10^{-4} M$  in this study, but any concentration from  $10^{-6} M$  to  $10^{-3} M$  is feasible in 1.0 M perchloric acid and 0.75 M sulfuric acid. Concentrations of  $10^{-7} M$  molybdenum have been detected in pure 5 to 7 M perchloric acid.

#### APPARATUS AND MATERIALS

A Sargent Heyrovský polarograph, Model XII, was employed throughout. An H-cell (4) was used, a saturated calomel electrode serving as the large, nonpolarized electrode.  $m^{2/3} t^{1/6}$  for the dropping mercury electrode was  $1.375 \text{ mg}.^{2/3} \sec.^{-1/2}$ . All polarograms were made at  $25 \pm 0.5^{\circ}$  C. Reagent grade granulated zinc was coated with mercury by displacement from mercuric sulfate solution. Reagent grade perchloric acid (70 to 72%) was diluted and standardized with sodium carbonate.

## PROCEDURE

The steel sample (0.05 to 1.0 gram) is dissolved in 15 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid in a 600-ml. beaker on a medium hot plate. When solution is complete, it is cooled, an excess of concentrated sulfuric acid is added, and the solution is evaporated to the last faint fumes of sulfur trioxide. Baking the residue renders the sample difficult to redissolve and should be avoided. Assuming the residue to be ferric sulfate, just enough sulfuric acid is added to make the concentration of sulfate 0.75 M in the final solution to be polarographed. The amount of sulfuric acid added will depend on the size of the original sample. Then 50 ml. of water are added and boiled 15 minutes, and the residue is worked with a rubber policeman to ensure complete solution of soluble material. The solution is filtered, if necessary, to remove insoluble material such as silica, tungstic oxide, and carbon. The filtrate is evaporated to to cover the bottom of the beaker and about one fourth of the perchloric acid to be added subsequently to prevent reduction of molybdenum to the trivalent form. The solution is swirled vigorously until reduction of the iron to ferrous appears complete or nearly so, then decanted away from the zinc. Enough perchloric acid is added to make the final solution 1 M and diluted to 50 ml. Air is removed with nitrogen and the solution is polarographed.

Results obtained by this procedure, together with those obtained by the National Bureau of Standards using other procedures, are shown in Table V.

Table V. Determination of Molybdenum in Iron and Steel

		Molybdenum, %		
Sample		NBS results	Polarographic results	
4g 30d 72d 123a 132 820	Cast iron Cr-V steel Cr-Mo steel Cr-Ni-Cb steel Mo-W-Cr-V steel Ingot iron	$\begin{array}{c} 0.017 \pm 0.002 \\ 0.034 \pm 0.002 \\ 0.210 \pm 0.005 \\ 0.12 \\ 7.07 \pm 0.07 \\ 0.002 \end{array}$	$\begin{array}{c} 0.018, 0.017, 0.0195\\ 0.031, 0.032, 0.034\\ 0.217, 0.222, 0.228\\ 0.127, 0.102, 0.123\\ 7.07, 6.91, 6.96, 7.10\\ 0.002, 0.002, 0.001 \end{array}$	

## NOTES ON PROCEDURE

Conversion to sulfate makes possible strict control of anion concentrations other than perchlorate. Reduction with zinc eliminates possible interference from other metal ions by removing them or reducing them to a low valence state which does not interfere. It is possible to reduce molybdenum to the trivalent state, which leads to low results. Addition of some perchloric acid at this point prevents formation of trivalent molybdenum. Air will generally reoxidize the small amounts involved very quickly. If a small amount of ferric iron remains (up to 10

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times the molybdenum concentration) it does not interfere and ensures that molybdenum is not in the trivalent form. The only difficulties with overreduction of molybdenum if no perchloric acid is added during reduction with zinc occurred with the sample containing 7% molybdenum, and with a sample containing 11% chromium. Chromous ion seems to hinder the reoxidation of molybdenum(III). The presence of perchloric acid during the reduction prevented low results in each case.

Experiments with the reduction of molybdenum with zinc in the presence of perchloric acid indicate that molybdenum(III) is not produced until the perchlorate is virtually all reduced to chloride. Thus if the solution is removed from the zinc as soon as the iron appears reduced, very little perchloric acid will be attacked and it is certain that molybdenum is not reduced beyond the pentavalent state. The concentrations of perchlorate and sulfate were selected arbitrarily for convenience. The analyst may use any concentrations he chooses, so long as they are carefully regulated. It is recommended, however, that the concentration of perchlorate be at least 0.1 M and that it be the predominant anion in the solution.

Work is in progress in this laboratory to determine whether this effect can be applied to the determination of chlorates and perchlorates as well as molybdenum, and to learn the mechanism of this reduction, which seems to be very specific for molybdenum.

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## Ceric Sulfate-Arsenious Acid Reaction in Microdetermination of Iodine

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THE reaction between ceric sulfate and arsenious acid was first applied to the determination of iodides by Sandell and Kolthoff (11, 12) and subsequently adapted to the microdetermination of iodine in biological materials (1-4, 7-10, 13, 14). [In acid solution, ceric sulfate forms sulfatoceric acid with the cerium in the anion ( $\beta$ ). In this report, however, cerium in both oxidized and reduced forms is considered cationic.] The basic reaction, catalyzed by soluble iodides, involves the reduction of ceric ion by arsenite ion in an acid medium:

$$2\mathrm{Ce}^{++++} + \mathrm{AsO}_3^{---} \longrightarrow 2\mathrm{Ce}^{+++} + \mathrm{AsO}_3^{-} \tag{1}$$

The reduction of the yellow ceric to colorless cerous ion is usually followed photometrically, and a series of empirical standardization curves relating photometer readings to known quantities of iodide at predetermined reaction times is employed. Attempts to use these procedures in this laboratory for the determination of serum iodine yielded erratic results, indicating that a reinvestigation of the method was required. As none of the previously published methods takes advantage of the velocity constant as a measure of catalysis by iodide, this possibility was investigated, and studies on the light-absorption characteristics of ceric sulfate solutions and on the kinetics of the oxidation-reduction reaction were required.

#### LIGHT-ABSORPTION CHARACTERISTICS OF CERIC SULFATE SOLUTIONS

Ceric sulfate solutions absorb maximally in the ultraviolet range at about 315 m $\mu$ , and in this region absorption seems to behave in accordance with Beer's law (5, 15). However, as most photometers are not useful at this wave length, light at the blue end of the visible spectrum is employed. Chaney (3) presents a curve which indicates that at 420 m $\mu$  the absorption characteristics of ceric sulfate solutions deviate considerably from Beer's law. Salter (8-10), at the same wave length of light, uses Klett photometer readings (directly proportional to optical density) to express concentration of ceric solutions and thereby implies conformity with Beer's law.

A Coleman Universal spectrophotometer with light at a wave length of 420 m $\mu$  was used with cuvettes consisting of 20  $\times$  150 mm. borosilicate glass tubes, selected for uniform optical properties. Selection was made by measuring at 420 m $\mu$  the percentage light transmittance of a solution of  $5 \times 10^{-4} M$  ceric sulfate [Ce(HSO<sub>4</sub>)<sub>4</sub>] in 3.6 N sulfuric acid; cuvettes that did not agree within 0.5% transmittance were rejected. As acidity and temperature were found to influence the optical density of ceric sulfate solutions, these factors were controlled at the levels used in studying the reaction. Accordingly, a series of ceric sulfate solutions was prepared: To each cuvette were added 2 ml. of 2 N sodium carbonate, 2 ml. of 7 N sulfuric acid, various quantities of ceric sulfate, and sufficient water to bring the total volume to 10 ml. (This method is intended for use in the determination of serum protein-bound iodine; the sodium carbonate represents the residue from an alkaline dry-ashing procedure. An equivalent excess of sulfuric acid is also included.) The cuvettes were then placed in a constant temperature water bath at 40° C., and finally read in the spectrophotometer at 420 m $\mu$ .

The results disclosed a curvilinear relationship between optical density and concentration, confirming the reported (3) deviation from Beer's law. The curve describing this relationship is a hyperbola, rectifiable by plotting the reciprocals of both variables.



As in the measurement of velocity constants the logarithm of concentration of reactants is required, it was found convenient to plot percentage light transmittance against log concentration of ceric sulfate. This resulted in an S curve, the central portion of which was linear (Figure 1). In order to exclude the nonlinear portion of the curve, and to remain well within the accurate range of the photometer, transmittance readings were subse-