

mechanically with a spatula and washed with a jet of water. Otherwise, it may be removed just by washing. Glass fiber filter paper may be used in the first extraction of the ore with nitric acid. This increases the ease of removal of the residue from the crucible; however, these residues cannot be stirred while washing with hot water; thus, the number of washings has to be increased.

By using a supporting electrolyte containing approximately 6*N* hydrochloric acid, few ions interfere with the tungsten wave. Over 30 of the more common cations were tested for possible interfering effects by adding small quantities of the cations in their various oxidation states to 100 ml. of constant-boiling hydrochloric acid and observing whether a polarographic wave was obtained in the region of the tungsten wave. Waves produced by nickel, vanadium, tin, lead, copper, arsenic, and molybdenum were found that were close enough to the tungsten wave to have possible interfering effects. Aluminum, silver, gold, boron, barium, bismuth, calcium, cadmium, cobalt, chromium, iron, mercury, magnesium, manganese, phosphorus, platinum, rhodium, antimony, strontium, titanium, uranium, zinc, and zirconium were not expected to interfere in this analysis and did not give waves close to the tungsten wave in the supporting electrolyte used here.

Nickel, vanadium, lead, copper, arsenic, and molybdenum are separated from tungsten by extracting the ore with concentrated nitric acid. Tin remains in the ore and is thus separated from the tungsten as it is not extracted by either concentrated nitric acid or concentrated hydrochloric acid. Small amounts of these interfering elements can be tolerated in the final solution used for polarographic analysis, although it is believed that the separation of these elements from the tungsten is quantitative. One tenth of a gram of each of the above-mentioned elements in their various oxidation states were mixed and added to a standard sodium tungstate sample. Using the procedure employed here for tungsten, a value of 4.09 was obtained for i_d/C for the tungsten wave, which indicated that these elements do not interfere.

The values of i_d/C for the tungsten ores containing 0.004 to 0.06% tungstic oxide show an excellent reproducibility for a given sample with an average value of 4.15 for the 49 determinations made in this concentration range (see Table I). The average value of i_d/C for 22 standard sodium tungstate solutions in the supporting electrolyte used here was 4.19 over a similar equivalent concentration range of tungstic oxide in the ores.

The polarographic procedure for the determination of small quantities of tungsten in ores as developed here requires about

half the time of the gravimetric procedure, has a better precision as shown in Table I, and has a better accuracy especially in the low grade ores as shown by the use of sodium tungstate as a standard. The preparation of the final solution for the colorimetric analysis developed by the Climax Molybdenum Co. requires about as much time as the preparation of the solution used in the polarographic analysis. The precision and accuracy for the polarographic method are better than those for the colorimetric method in the low grade ores, but not as good in the high grade ores. They are not as good as in the gravimetric method for ores containing more than 10% tungstic oxide, because no better than the usual polarographic precision of 1 to 2% can be expected in any concentration range for a given sample.

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Determination of Molybdenum by Ion Exchange and Polarography

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A method for determining molybdenum, particularly in steels, is based on polarographic reduction of molybdenum(VI) in 0.1*M* sulfuric acid-0.5*M* citric acid. Well formed doublet waves are obtained for the reduction to molybdenum(V) and (III). Diffusion currents are directly proportional to concentration, but slightly dependent on pH and ionic strength. A standard addition technique eliminates careful control of experimental conditions and nonlinear calibration curves. All interfering cations are removed with an ion exchange resin. The final solution contains only molybdate and possibly tungstate and the supporting electrolyte. NBS steel samples have been analyzed with relative errors of less than 3%.

THE polarographic determination of molybdenum has been difficult because of the lack of a suitable supporting electrolyte in which the waves are well formed with the diffusion current proportional to concentration. Holtje and Geyer (4), von Stackelberg and others (9), Stepien (10), and Carritt (1) have discussed the molybdenum waves occurring in highly acidic solutions. Analytically useful waves are obtained in solutions containing 10*N* or more sulfuric acid, and have been used for the determination of molybdenum in steels. However, von Stackelberg's procedure (9) involves its prior separation as molybdenum disulfide and conversion to molybdenum trioxide by a time-consuming series of steps. Stepien's procedure (10) involves its separation as molybdenum trisulfide and conversion to sulfo-molybdate followed by determination in 18*N* sulfuric acid. Parry

and Yakubik (7) have described a method for steels using a tartaric acid supporting electrolyte; however, the method was tested on composited solutions and not actual steel samples.

The perchlorate wave produced in the presence of molybdenum has been utilized by Haight (2) for iron and steel samples. The method requires careful control of anions and the wave is not proportional to the concentration of molybdenum. A nonlinear calibration curve must be prepared for each set of conditions.

A rapid polarographic determination of molybdenum in the presence of large amounts of tungsten was described by Meites (6), based on the wave produced in citrate buffers at pH 7. However, the result must be obtained from a nonlinear calibration curve. The method was not applied to samples other than reagent grade sodium tungstate.

The separation of molybdate from all interfering cations by ion exchange has been described by Klement (5), who completed the determination gravimetrically. Volumetric methods failed, as did most common precipitating reagents, but good results were obtained with 8-quinolinol.

This paper describes a method applicable to a wide variety of samples. The molybdate is separated by a simple ion exchange technique. The determination is made from the polarographic wave obtained in a 0.1M sulfuric acid-0.5M citric acid solution. In this medium the double wave is well formed and the diffusion currents are directly proportional to the concentration of molybdenum. The diffusion current constant is somewhat dependent on pH and ionic strength, but with the dilution technique proposed, none of the conditions are critical.

EXPERIMENTAL

A stock solution of sodium molybdate (0.1M) was standardized by redox titration using a Jones reductor and standard permanganate (3). All chemicals were reagent grade. The ion exchange column was prepared in a 50-ml. Kimble Exax buret, and contained about 20 ml. of analytical grade Dowex 50-X12, 50- to 100-mesh cation exchange resin supported on glass wool. Polarograms were recorded on a calibrated Sargent, Model XXI, polarograph using a three-compartment cell (8). Measurements were made at $25^\circ \pm 0.1^\circ$ C. The capillary had a flow rate of 1.45 mg. per second and a drop time of 5.55 seconds at an applied potential of -0.2 volt. Solutions were deaerated with purified nitrogen and no maximum suppressors were added. All potentials were measured and reported *vs.* the saturated calomel electrode.

All pH measurements were made with a Beckman, Model G, pH meter.

PREPARATION OF SAMPLE

Samples which do not contain tungsten can be readily dissolved in dilute sulfuric acid, provided some ammonium persulfate is added after the initial reaction subsides. The persulfate oxidizes molybdenum, chromium, vanadium, manganese, and iron to their highest oxidation states. In order to reduce the chromium, vanadium, and manganese, which are anionic after the dissolution, to stable cations, a small amount of sodium bisulfite is added and the excess sulfur dioxide is boiled off. Citric acid is added for the dual purpose of keeping the molybdate in solution in the acidic medium and for its effect on the subsequent polarogram.

The solution is then made up to a known volume and poured through the ion exchange column which has been previously rinsed with 0.5M citric acid solution. The first 10 to 15 ml. of the filtrate is discarded, after which the filtrate is essentially uniform in composition until the breakthrough of the large amount of iron in the sample. The use of a buret for the column facilitates the measurement of exactly 10 ml. of the filtrate into the polarographic cell. It is not necessary to run the entire sample through the column; therefore, the capacity of the

resin can be safely reduced or the rate of flow can be increased.

Samples containing tungsten are dissolved in dilute hydrochloric acid followed by the minimum amount of concentrated nitric acid required to oxidize the metals to their highest oxidation state. The nitric and hydrochloric acids are then removed by fuming in the presence of sulfuric acid. The remainder of the procedure is the same as above.

PROCEDURE FOR STEEL SAMPLES

Weigh the sample (0.1 to 0.5 gram if more than 1% molybdenum; 0.5 to 1.0 gram if less than 1% molybdenum) into a tall-form 200-ml. beaker.

Samples without Tungsten. Add 5 ml. of 6N sulfuric acid and cover beaker with a watch glass. Warm gently on a hot plate until the reaction diminishes. Add 1 gram of ammonium persulfate and boil gently for 10 minutes.

Samples with Tungsten. Add 10 ml. of 6N hydrochloric acid and cover with a watch glass. Warm gently on a hot plate until the reaction subsides. Add 1 to 2 ml. of concentrated nitric acid and heat to boiling. Evaporate to incipient dryness. (The use of an infrared lamp prevents bumping.) Add 10 ml. of 6N sulfuric acid and again evaporate to incipient dryness. Dissolve the residue in 5 to 10 ml. of 6N sulfuric acid.

Table I. National Bureau of Standards Steel Samples

Sample No.	% Mo	Composition, %	% Mo Found	Av.	Error, %
111b	0.255	0.706 Mn, 1.81 Ni 0.028 Cu, 0.070 Cr 0.043 Al, 0.003 V	0.254, 0.254 0.278, 0.259	0.261	+2.4
159	0.414	0.807 Mn, 0.137 Ni 0.181 Cu, 1.00 Cr 0.090 Ag, 0.054 V	0.424, 0.432 0.441, 0.440	0.434	+4.9
106a	0.203	0.546 Mn, 0.277 Ni 0.156 Cu, 1.15 Cr 1.08 Al, 0.002 V	0.195, 0.196 0.202, 0.197	0.198	-2.4
50b	0.401	0.325 Mn, 0.089 Ni 0.110 Cu, 4.08 Cr 1.02 V, 18.05 W	0.430, 0.420 0.417, 0.371 0.410	0.410	+2.2
123a	0.12	0.75 Cb, 0.02 Ta 0.11 W, 0.037 V	0.113, 0.129 0.125, 0.114	0.120	0
36a	0.92	0.432 Mn, 0.243 Ni 0.114 Cu, 2.41 Cr 0.011 Sn, 0.006 V	0.89, 0.93 0.92, 0.92 0.92, 0.94	0.92	0
132a	4.50	0.27 Mn, 0.14 Ni 0.12 Cu, 4.21 Cr 6.20 W, 1.94 V	4.62, 4.55 4.65, 4.40	4.55	+1.1
153	8.38	0.219 Mn, 0.107 Ni, 4.14 Cr, 8.45 Co 1.58 W, 2.04 V	8.85, 8.15 8.88, 8.20	8.52	+1.7

If the sample contains a high percentage of tungsten—e.g., NBS 50b in Table I—and does not dissolve with procedure of samples with tungsten, some molybdenum will be retained by the tungstic acid precipitate. To avoid this loss, add 10 grams of sodium citrate and sufficient sodium hydroxide to dissolve the tungstic acid upon gentle boiling. The sample may then be acidified with sulfuric acid without danger of reprecipitation.

Dilute to 50 ml. with water and add 0.1 gram of sodium bisulfite. Boil until the odor of sulfur dioxide can no longer be detected. Add 7 grams of citric acid and 3 grams of sodium citrate. The pH should be between 1 and 2. Transfer to a 100-ml. volumetric flask, filtering if necessary to remove silica and carbon. Make up to the mark.

Pour several 2- to 3-ml. portions of the solution into the ion exchange column, allowing each portion to drain to the top of the resin. Discard the first 10 to 15 ml. of the filtrate. Fill the column to the zero mark on the buret and allow the next 10.00 ml. to run into a dry polarographic cell. Record the polarogram from $+0.2$ to -0.5 volt. Add exactly 1.00 ml. of a standard sodium molybdate solution to the 10 ml. of test solution in the cell. (The concentration of the standard molybdate solution should be such that the addition approximately doubles the concentration of molybdenum in the cell. For accurate work the standard should contain 0.1M sulfuric acid and 0.5M citric acid.) Record a second polarogram and measure the diffusion

currents of the first wave. The result may be obtained from the formula:

$$P = \frac{100 M V_0 V_s C_s i_1}{S(i_2 V_1 + i_2 V_s - i_1 V_1)}$$

where P is the per cent of molybdenum in the sample, M is the atomic weight of molybdenum, V_0 is the volume in milliliters to which the sample is made up, V_1 is the volume in milliliters of the sample solution in the polarographic cell, V_s is the volume in milliliters of standard solution added, C_s is the molar concentration of the standard solution, S is the sample weight in grams, and i_1 and i_2 are the heights of the polarographic waves before and after the addition of the standard, respectively. Using the standard procedure described above, the formula reduces to:

$$P = \frac{96000 C_s i_1}{S(1.1 i_2 - i_1)}$$

RESULTS

These procedures have been tried on synthetic samples containing large amounts of chromium, vanadium, copper, nickel, tungsten, manganese, and cobalt with satisfactory results.

The results obtained on National Bureau of Standards steel samples are shown in Table I.

POLAROGRAPHIC DATA

The polarograms of molybdenum in dilute sulfuric acid (pH 1), with and without the addition of citric acid, are shown in Figure 1. A detailed discussion of the polarographic behavior of molybdenum in this medium is beyond the scope of this paper and will be submitted elsewhere. Other hydroxy acids—e.g., tartaric acid and gluconic acid—have the same effect on the wave as does citric acid, and it would appear from the work of Strickland (11) that the numerous polynuclear complexes present in dilute sulfuric acid are changed into simple complexes in the presence of citric acid. The exact nature of this complex has not yet been elucidated.

The ratio of the two waves is approximately 1 to 2, indicating that reduction proceeds from the +6 state to the +5 state, and then further to the +3 state. Either wave may be used in a determination. At concentrations greater than $10^{-4}M$, the first wave can be measured more accurately and is less subject to

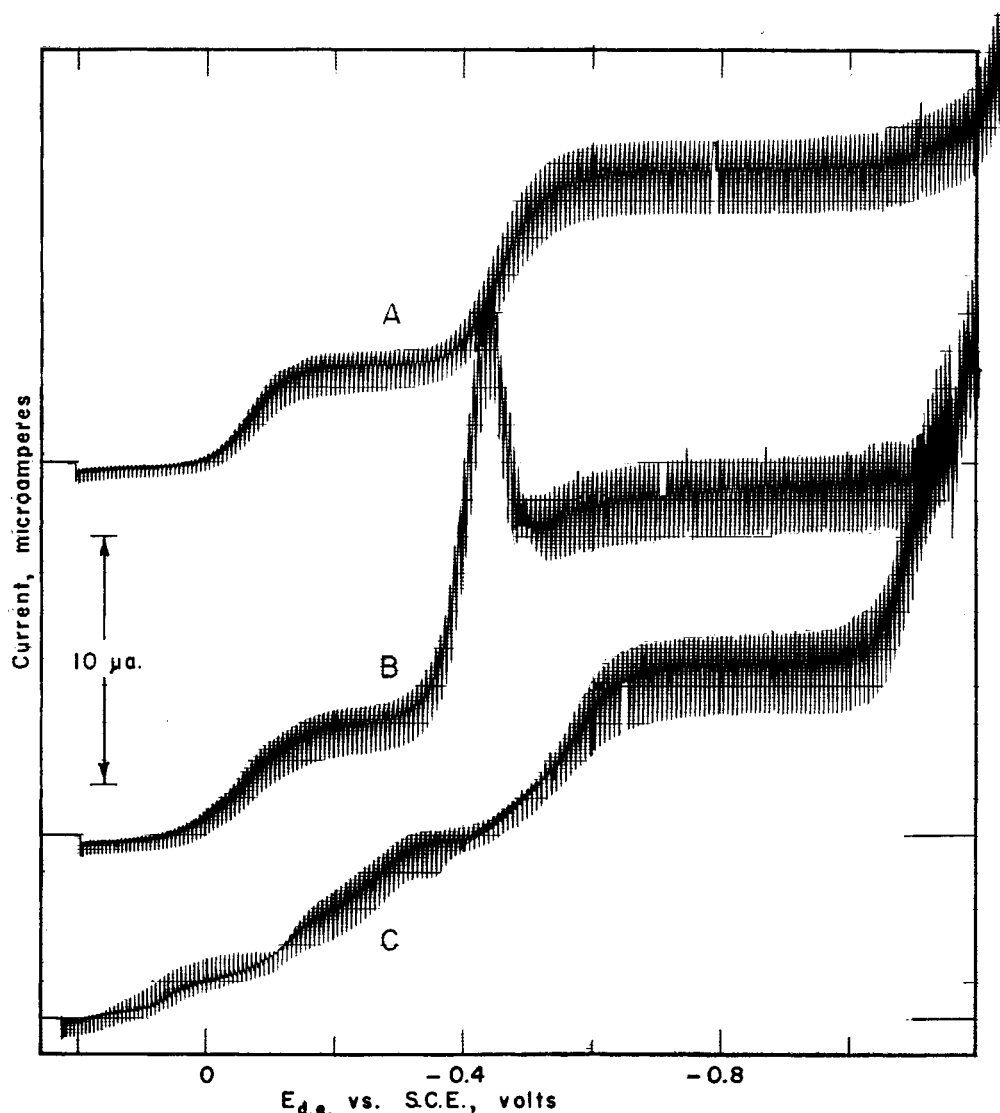


Figure 1. Polarograms of 1mM molybdenum(VI) in 0.1M sulfuric acid

A. With 0.5M citric acid
B. 0.05M citric acid
C. No citric acid
Solutions adjusted to pH 1

interference from tungsten than the second. Tungstate is not reducible in this medium when present alone. In the presence of tungstate, the second molybdenum wave does not become parallel to the residual current line but continues to increase. In solutions more dilute than $10^{-4}M$, the uncertainty of the residual current makes it preferable to use the second wave.

The half-wave potentials of the two waves in $0.1M$ sulfuric acid– $0.5M$ citric acid, pH 1, are -0.070 and -0.430 volt, respectively. The first wave is reversible in $1M$ sulfuric acid– $0.5M$ citric acid, but becomes increasingly irreversible as the pH is increased or the citric acid concentration is decreased.

The diffusion current constant, I , is 1.50 for the first wave and 3.04 for the second wave ($m^{2/3}t^{1/6} = 1.965$). These values of I increase slightly with acidity and decrease with ionic strength; however, under any given conditions, the diffusion current is exactly proportional to concentration of molybdenum in the range 10^{-4} to $5 \times 10^{-3}M$. In order to simplify the procedure and increase the accuracy, a standard addition technique is proposed in which a known amount of molybdenum is added to the sample solution and a second polarogram taken.

Both nitrate and perchlorate yield large catalytic waves which interfere with the measurement of the molybdenum wave and must be removed if present. Chloride ion must not be present in large amounts because the anodic dissolution of mercury to

form calomel masks the first molybdenum wave. In the procedure given, none of these anions need be present.

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Simplified High Temperature Sampling and Use of pH for Solubility Determinations

System Uranium Trioxide–Sulfuric Acid–Water

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The solubility of uranium trioxide in aqueous sulfuric acid at elevated temperatures, 150° to 290° C., has been determined by directly sampling a solution equilibrated with solid uranium trioxide hydrate at the respective temperatures and comparing the pH of the isolated sample at 25° C. with control pH data. Isotherms of the solubility of uranium trioxide hydrate in aqueous sulfuric acid have been obtained from 1.0 to 0.00023 molal acid. In the apparatus designed for solubility determinations particular solutions are sampled with rapidity and ease. The solution sample is delivered at room temperature, but removed from the saturated solution at the equilibration temperature. This sampling method is reproducible and apparently reliable. The control pH data of uranium trioxide–sulfuric acid–water solutions at $25.00^{\circ} \pm 0.04^{\circ}$ C. have been determined to a precision within ± 0.004 pH unit from 0.024 to 0.00024 molal sulfuric acid. These data have been obtained by the use of a vibrating reed electrometer and accessory equipment.

THE purpose of this investigation was to obtain experimental solubility data in the dilute region for the system, uranium trioxide–sulfuric acid–water, at elevated temperatures and, in so doing, to devise a method for sampling an equilibrated solution intermittently with rapidity and ease. In designing the pressure bomb for containing solutions the interior volume had to be kept relatively small in order to minimize the bulk size necessary to withstand pressures of approximately 1246 pounds per square inch at 300° C.

The bomb contained a length of thin-walled capillary tubing attached at one end to a pressure valve equipped with a sampling

tip. The other end of the capillary passed through the bomb head and was inserted into the equilibrated solution. Part of the capillary between the bomb head and the pressure valve passed through a wet ice bath. By means of this design the solution was rapidly cooled during the sampling process, thereby eliminating a separate cooling or isolation chamber and facilitating the procurement of many samples per run. This method appears more advantageous than the "one sample per experiment" filter bomb method which relies either on a difference in vapor pressure between two internal cells or on gravitational flow to accomplish filtration at or near the equilibration temperature (2, 3). In the use of a vapor pressure difference there is an uncertainty whether solvent distills to the filtrate during the filtering process. With the direct sampling technique there is neither a distillation problem nor a need for correction for loss of solvent or other components to the vapor phase at the equilibration temperature, as the liquid phase alone is sampled at the elevated temperature and can be analyzed for all components. However, with systems having a positive temperature coefficient of solubility the precipitation characteristics and solubility range of the individual system would have to be considered and evaluated.

Solid phase particles might be withdrawn through the capillary during the sampling process. In the system under study, the uranium trioxide hydrate settles rapidly (within seconds) at the high temperatures, leaving a clear liquid from which the sample is obtained. This settling action has been observed visually by means of the semimicro-phase study apparatus (10). Also, because the dissolving rate of uranium trioxide solid is sufficiently slow, any solid which may be withdrawn can be seen in the liquid sample. No solid was observed. If settling rates are slow for other systems, a filter may be attached to the tip of the capillary tubing within the bomb.