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A Thesis

Submitted to the Department of Metallurgy
in partial fulfillment of the
requirements for the Degree of
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PURPOSE OF INVESTIGATION

In the past germanium has been determined by either wet methods or by the spectograph; the spectograph being used for the determination of very small amounts of germanium and wet methods used when more than one hundredth of one percent germanium is present. Both of these analytical schemes have weaknesses. The spectograph does not always work, for the presence of low potential elements results in a very weak spectrum, and wet methods are not accurate when less than one hundredth of one percent germanium is present. These weaknesses have prompted investigations for new analytical schemes for the determination of germanium.

The polarograph has been applied to a large number of chemical and metallurgical analyses, and is especially applicable to solution control analysis and to the determination of minute quantities of ions in the presence of large amounts of other ions.[1] These features make polarography a possiable answer to an analytical scheme for germanium and have prompted this research.

HISTORY

It has been proved by I. P. Alimarin and B. N. Iwanow Emin that quadra-valent germanium compounds are not reduced by the electrolysis on the dropping mercury cathode in acid and alkali solutions and in the presence of complex-forming hydrofluoric and oxalic acids, while bi-valent germanium compounds are easily reduced to metal. This polarographic analytical method gives a possibility to detect and to estimate quantitatively the germanium content in acid solutions at dilutions of one part in one million.[2] To the writer's knowledge at this date the above is the only work that has been done on a polarographic method for the determination of germanium.

LABORATORY PORCEDURE

Standard solutions of germanium were made up by dissolving germanium dioxide with a small amount of water and caustic, and diluted up to a known volume with water. Aliquots of these solutions were taken to be analysed on the polarograph. Burettes were used to measure all solutions and analytical balances used to measure all solids. An aliquot of the standard was placed in a twenty-five milliliter wolumetric flask with one and six tenths grams of sodium hypo phosphite, six tenths of a milliliter of two percent gelatin solution, brought to six normal with conc-intrated hydrochloric acid, and diluted to volume with six normal hydrochloric acid. This solution was then heated in a water bath at from fifty to sixty degrees centigrade for one half of an hour and placed in a polarizing cell. The solution was then deoxidized bypassing nitrogen gas through it for a period of five minutes. A polarogram was taken within one hour of heating.

LABRATORY RESULTS

In this investigation of a polarographic determination of germanium it was found that in order to obtain a uniform germanium polarogram that the following things must be taken into consideration: the amount of reducing agent necessary to reduce all of the germanium from a plus four valende to a plus two valence, the temperature at which the above

reaction takes place, the time necessary to complete this reaction, the time of gassing to prevent the formation of an oxygen manima, the amount of gelatin to prevent the formation of a maximum, the length of time lapsed before taking the polarogram, the drop time of the dropping mercury electrode, and the temperature of the solution while making the polarogram. The drop time and temperature of the solution while making the polarogram were fixed at one drop every three to four seconds and twenty to twenty-two degrees centigrade.

The first step was to verify the works of I. P. Alimarin and B. N. Iwanow-Emin that quadra-valent germanium compounds are not reduced by the dropping mercury electrode. This was done by dissolving germanium with sodium carbonate and water and making the resulting solution up to six normal with concetrated hydrochloric acid and making a polarogram with this solution. The results of this polarogram were two fold; it showed that the solution containing germanium in the plus four valence gave exactly the same curve as the blank, and that a maximum was formed on the hydrochloric acid curve. This maximum was easily removed by relacing the oxygen in the solution with nitrogen.

The second step was to prove that bi-valent germanium could be reduced at the dropping mercury electrode. In order to accomplish this a very strong reducing agent which will not be reduced at or near the same potential as germanium oxide was needed. An example of a strong reducing agent that cannot be

used is stanic chloride, since tin has very nearly the same deco position potential as germanium. I. P. Alimarin and B. N. Iwanow-Emin found that sodium hypo phosphite could be used, but up until a few weeks before this work was completed pure sodium hypo phosphite was not available.

For the early part of the work crude sodium hypo phosphite made by reacting yellow phospherous with sodium hydroxide. This reaction takes a great deal of time and and is very dangerous since both phospherous and the resluting phosphine gas are explosive on contact with air. The procedure used was as follows: A solution of sodium hydroxide was placed in a one thousand millileter florence flask and the air was replaced by passing nitrogen through the flask. Phospherous was then added intermittently and the solution brought just below its boiling point until no more phosphine gas was emitted. The phosphine gas emitted was allowed to bubble through a water bath and ignite on contact with the air; The water baths purpose was to prevent air from flowing back into the florence flask if for any reason the solution cooled too rapidly and formed a vacure in the flask.

This crude sodium hypo phosphite in six normal hydrochloric acid was tested on the polarograph to see if it or any impurities in ities in it would decompose. The resulting polarograms showed no wave indicating that the reducing agent could be used as it was.

A solution containing one hundred milligrams of germanium was made up by diss-olving germanium di-oxide in sodium hydroxide and making up to five hundred millileters with water, sodium hypo phosphite was added and the resulting solution run on the polarograph. The polarogram showed no wave was formed, so more sodium hypo phosphite was added and a polarogram recorded; the polarogram showed a wave had been formed. This wave was no indication of how much germanium present in solution, but it did show that some germanium had been reduced to the plus two valence and that in this state germanium could be reduced at the dropping mercury electrode.

PRODUCTION OF A STANDARD CURVE

In order to use the polarograph for quantative analysis a procedure must be set up to produce a standard wave that will represent a certain amount of an element that is in solution. The remaining time was spent in producing a reproduciable curve.

Amount of Sodium Hypo Phosphite

Having found that sodium hypo phosphite will reduce germanium from the plus four valence to the plus two valence and since the strength of the crude sodium hypo phosphite could only be approximated, it was necessary to secure pure sodium hypo phosphite in order to regulate the amount necessary to produce a standard curve.

Using pure sodium hypo phosphite, a six normal
hydrochloric acid solution, and the assumption that one
mole of sodium h̸y̸p̸ hypo phosphite would reduce one mole of
germanium, polarograms were taken of a solution containing
one hundred milligrams of germanium per liter. These
polarograms showed no wave. Assuming the above failure to
be caused by the lack of reducing agent a four hundred times
excess of sodium hypo phosphite was added; the resulting
polarograms showed that the germanium had been reduced but
they also showed that curves taken at different times were
of different heights and that a maximum was formed that could
not be surpressed by gasing.

Due to lack of time it was impossible to determine the
exact amount of sodium hypo phosphite necessary to produce a
reproducible wave and at the same time find a method for pro-
ducing a standard curve and supression of the maximum. So
the amount of sodium hypo phosphite was set at four hundred
times the theoretical amount or approximatly one and six
tenths grams per twenty-five millileters of solution.

Surpression of the Maximum

The foremost source of trouble in polarographic
analysis is the formation of maxima in the current-voltage
curves. The maxima are pronounced peaks occuring at the top
of the wave, and are so erratic that they cannot be evaluated

relative to the ion concentration. Probably the most generally effective suppressor and the simplest to use is gelatin. Most metalic maxima can be effectively suppressed by adding sufficient gelatin to bring its concentration to .001% but high concentrations of gelatin tend to suppress the limiting current.[1] It has also been established that the amount of gelatin should not exceed .005%.[3] Using this as a basis it was found that one milligram of gelatin in twenty-five milliliters of solution is enough to suppress the maximum/ this is .004% gelatin and within the limits for polarography. In order to make the addition of gelatin easier a standard two tenths of one percent gelatin solution was used and for twenty-five milliliters approximately six tenths of a milliliter is necessary. This small amount can be added without noticable effect on the normality of the electrolite.

Producing a Curve of Reproduciable Height

Germanium chloride is volitale at eighty-five degrees centigrade; therefore, %% in order to hasten the reaction of sodium hypo phosphite with germanium by heating, it was necessary to conduct this heating in a stoppered bottle. It was tetermined that in order to get a reproducible wave that this solution must be heated for thirty minutes at from fifty to sixty degrees centigrade. Whether the germanium

chloride is all maintained in the stoppered bottle or its loss is uniform is not known and should be determined in the future if this process is to be perfected.

Time of Taking Polarograms

The polarogram should be taken within one hour after it has been removed from the water bath, since after this time has lappsed the germanium starts to oxidize, and the height of the wave obtained will be noticeably smaller than if the polarogram is taken within one hours time.

DETERMINATION OF CALIBRATION CURVE

Using the procedure previously mentioned (page 3) solutions of one hundred milligrams per liter, fifty milligrams per liter, and twenty milligrams per liter of germanium were run on the polarograph. The results of these polarograms are shown on table I. On plotting the milligrams of germanium against the product of the wave height and shunt it was found that the points for the twenty milligrams per liter and the fifty milligrams per liter fall in a stright line with the zero reading, but the one hundred milligrams per liter solution does not. It is assumed that the one hundred milligrams per liter solution is biased. The reasons for this may be explained by several factors. It is possible that the temperature of the solutions while taking the polarograms was different for it was impossible to hold these
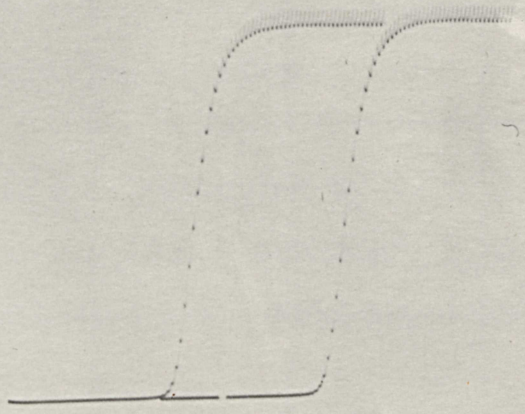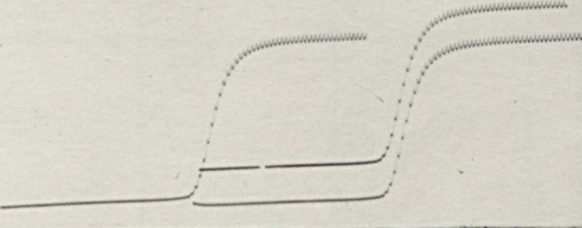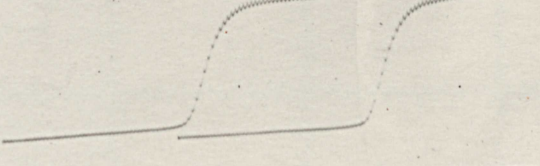
temperatures constant with the apparatus available. If
this was so the error is explained since a variation of
the temperature may cause as high as two percent error per
degree.   The graph can be seen on page 12.

Conclusion

A procedure has been described for the polarographic
determination of germanium that will work for pure solutions.
This procedure is by no means perfect and time should be
spent in smoothing it out, for once this procedure is worked
out it will not take too much effort to adapt it to commer-
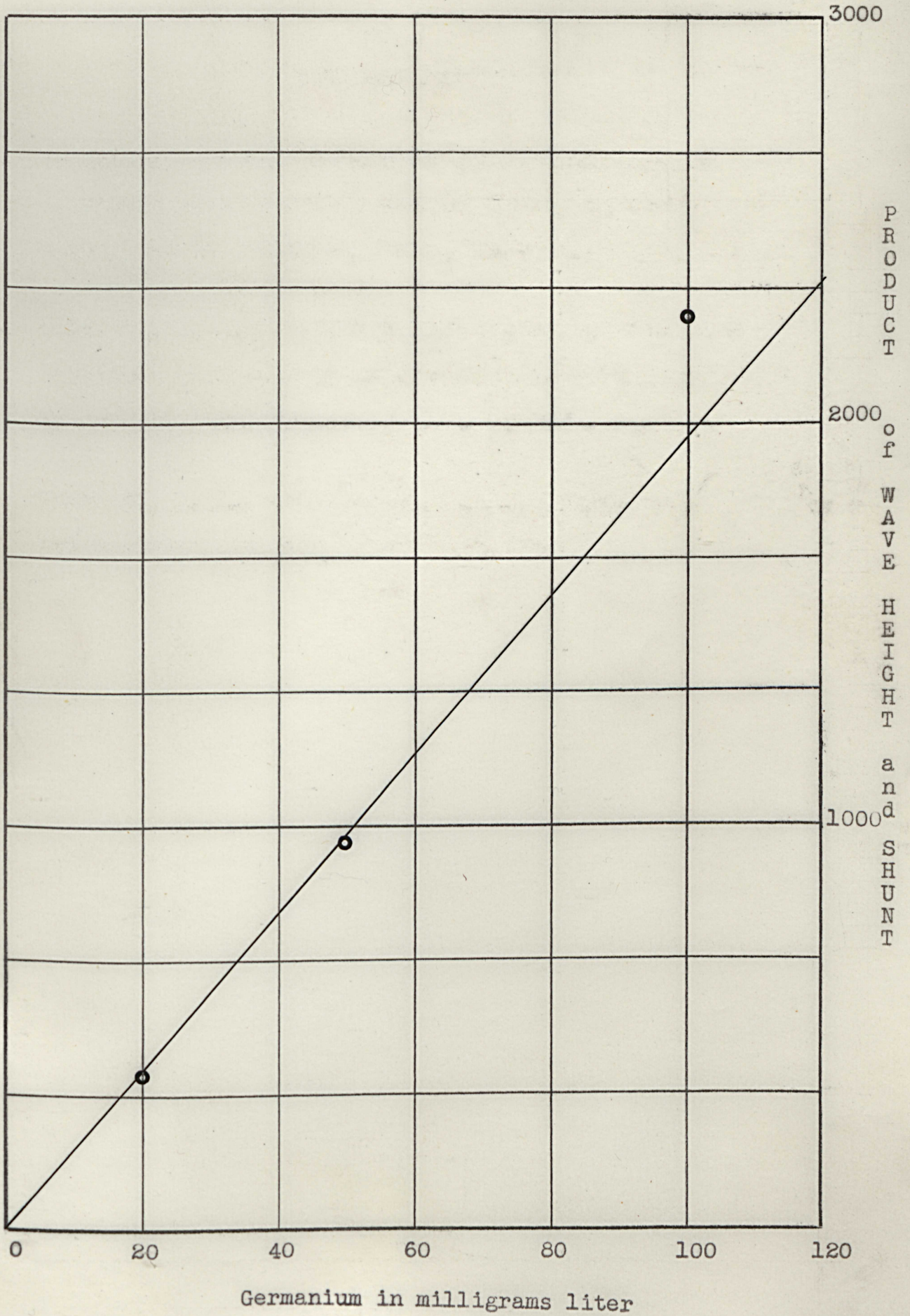cial products of both high and low germanium content.

TABLE 1

100 MG/LITER GERMANIUM 1.6 GM/25 ML SODIUM HYPO PHOSPHITE ELECTROLITE 6N HCL DROP TIME 1 DROP/ 3-4 SEC. SPAN .14-.5 VOLTS SHUNT 20 WAVE HEIGHT 11.3 MM.	
50 MG/LITER GERMANIUM 1.6 GM/25 ML SODIUM HYPO PHOSPHITE ELECTROLITE 6N HCL DROP TIME 1 DROP/3-4 SEC. SPAN .14-.5 VOLTS SHUNT 20 WAVE HEIGHT 4.8MM	
20 MG/LITER GERMANIUM 1.6 GM/25 ML SODIUM HYPO PHOSPHITE ELECTROLITE 6N HCL DROP TIME 1 DROP/3-4SEC. SPAN .14-.5 VOLTS SHUNT 10 WAVE HEIGHT 3.7MM.	

CALIBRATION GRAPH

Germanium in milligrams liter

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