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DETERMINATION OF FREE ACID IN  
SOLUTIONS OF URANYL SULFATE

O. Menis  
D. L. Manning  
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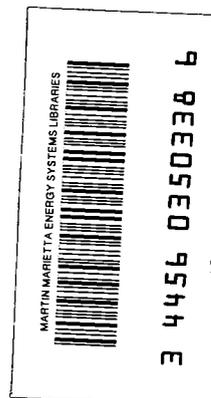
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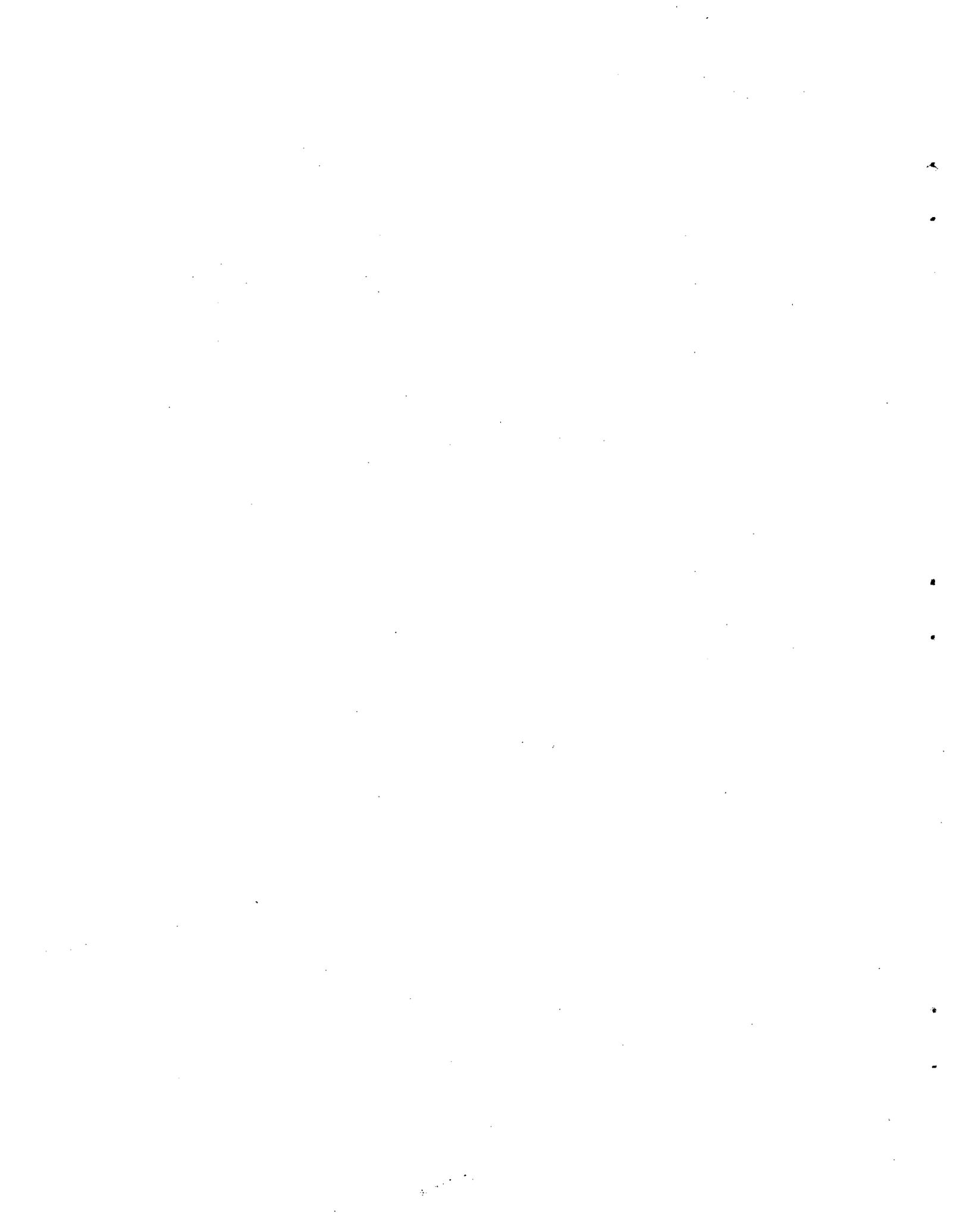
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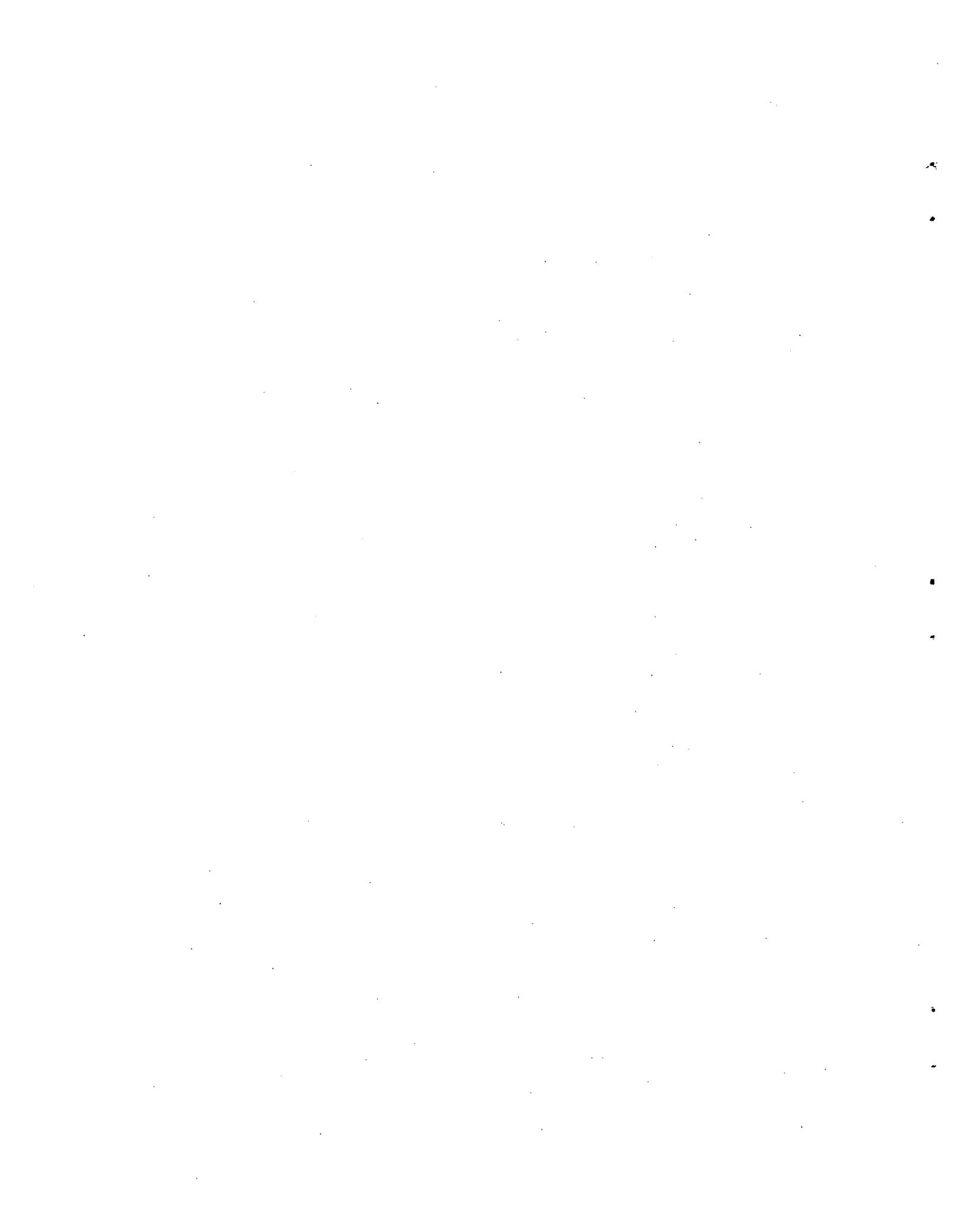
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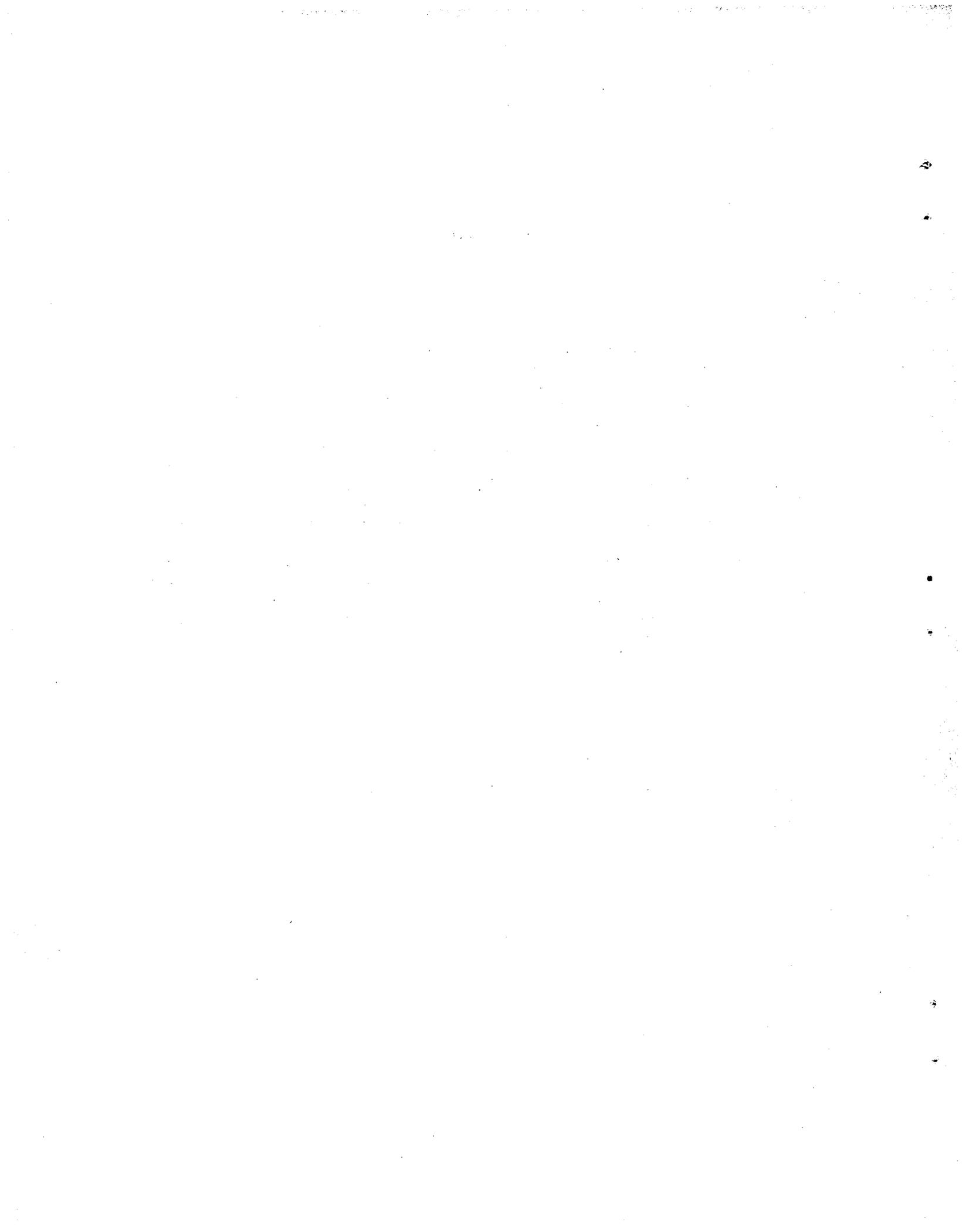
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ABSTRACT

A method is described for the determination of free acid in solutions of uranyl sulfate by means of the Sargent-Malmstadt Automatic differential titrator whereby the inflection point of a potentiometric curve is automatically detected and used to turn the buret off. This instrument has the advantage over other automatic titrators in that it does not require graphical interpretation of the end point or a pre-setting of the end point potential. The interference caused by the hydrolysis of uranyl ions was eliminated by complexing the uranium with fluoride. The electrode system of platinum-rhodium alloy indicator and calomel reference electrodes, used with this instrument, offered an advantage over a glass electrode system when titrating in a hydrofluoric acid medium. The application of this instrument offers a rapid and precise method for the determination of 0.1 to 1.0 milliequivalents of acid in the presence of 0 to 200 mg of uranium in a final volume of 50 ml. The coefficient of variation of the method is less than 2 per cent. When more than 200 mg of uranium is present, however, the coefficient of variation is of the order of 5 per cent.



## DETERMINATION OF FREE ACID IN SOLUTIONS OF URANYL SULFATE

Application of the Sargent-Malmstadt Automatic Differential Titrator

O. Menis, D. L. Manning, G. Goldstein

## INTRODUCTION

In the course of making analyses of solutions of uranyl sulfate, it was necessary to develop a rapid and precise method for the determination of the free acid in these solutions. Previous methods for the determination of free acid in the presence of any hydrolyzable material have involved direct measurements of the pH and a correction for the concentration of the hydrolyzed substances. Methods of titrating and subsequently correcting for the hydrolyzed salt have also been reported.<sup>(3)</sup> These methods, however, require an accurate knowledge of the quantity of hydrolyzable material that is present.

In general, three types of automatic titrators may be utilized for the potentiometric acid-base titration. An instrument such as the Dow recordomatic titrator, which records the potentiometric titration curve as a function of titrant volume, is an example of one type. The method that was being used in this laboratory prior to the development of the method that is reported herein involved titration by means of the Dow recordomatic titrator. The titration curve exhibits two inflection points. The first, which occurs at a pH of about 3.5, represents the neutralization of the free acid, whereas the second, which occurs at a pH of approximately 9, indicates the completion of the hydrolysis of the

uranium. The determination of the first end point from the titration curve is generally difficult since the first point of inflection is poorly defined due to the buffering action of the easily hydrolyzable uranyl ions. Therefore, the error in establishing the equivalence point of free acid titration is relatively large.

In a second type of titrator, the equivalence point potential is automatically anticipated, and the flow of titrant is terminated when this point is reached.<sup>(1,5)</sup> The use of this instrument requires that an accurate knowledge of the potential at the end point be known and that a presetting of the instrument to this potential be made prior to the titration. The utilization of this type of titrator to the determination of free acid in solutions of uranyl sulfate would be difficult since the potential at the end point would vary depending upon the amount of uranium present.

The third type of automatic titrator is the Sargent-Malmstadt automatic differential titrator. With this instrument, the inflection point of the potentiometric titration curve is determined automatically and the buret is turned off when this point is reached. This is accomplished by producing a voltage which is proportional to the second derivative of the potentiometric titrations curve; then this voltage is utilized to trigger a relay system which automatically stops the flow of titrant at this inflection point. Several advantages have been reported which characterize this instrument; namely, the equipment is simple, compact, and inexpensive; no presetting of the end point potential is necessary; various types of reference and indicator electrodes can be

used even though their absolute potentials shift from one titration to the next; and no instrument adjustments are required. (6,10)

In view of these seemingly inherent advantages, and especially since it would eliminate the need for estimation of the inflection point by graphical measurements, this instrument was utilized as a means of determining the free acid content of solutions of uranyl sulfate.

Preliminary tests on the application of the differential titrator to this problem revealed that the first end point, on neutralization of the free acid, was not detected by means of the instrument; instead, the titration was terminated automatically at the second end point, which occurred after the complete hydrolysis of the uranium. Apparently, the magnitude of the voltage change at the first point of inflection was not sufficient, due to the buffering action of the initial hydrolysis of uranyl ions, to activate the relay system which is used to terminate the flow of titrant.

In order to prevent the hydrolysis of the uranium, sodium fluoride was added to the solution to complex the uranyl ion. Sodium fluoride has previously been utilized as a complexing agent in the determination of free acids in the presence of hydrolyzable salts. (2,8) The studies carried out in the development of the new procedure were concerned with the optimum amount of sodium fluoride to use and the amount of uranium that can be tolerated. Finally, the precision of the method was evaluated.

## REAGENTS

1. Sodium Hydroxide, 0.1 N. Dissolve 4 g of reagent grade sodium hydroxide in 1 liter of distilled, carbonate-free water.
2. Sulfuric Acid, 0.1 N. Dilute 2.8 ml of concentrated, reagent grade sulfuric acid to 1 liter with water. Standardize the solution of sulfuric acid by titrating a solution of primary standard sodium carbonate with the acid.(9)
3. Sodium Fluoride, 15 mg of fluoride per ml. Dissolve 32 grams of reagent grade NaF in 1 liter of water.
4. Uranyl Sulfate, 10 mg of uranium per ml. Prepare by diluting 5 ml of a stock solution of uranyl sulfate that contains 500 mg of uranium per ml to 250 ml with water. Standardize gravimetrically by evaporating a 5-ml aliquot to dryness and igniting the residue to the oxide.

## APPARATUS

1. Sargent-Malmstadt automatic titrator, with stirrer, platinum-10 per cent rhodium, and saturated calomel electrodes; available from E. H. Sargent and Co., Chicago, Illinois.

## PROCEDURE

Standardization of the Sodium Hydroxide. Transfer 10 ml of the standardized solution of 0.1 N sulfuric acid to a 100-ml beaker. Add 10 ml of the solution of sodium fluoride; then dilute the sample to 40 ml with water. Titrate the solution with the sodium hydroxide titrant

to the automatic cut-off point of the differential titrator. Adjust the flow rate from the buret to 6 to 8 ml per minute.

Titration of the Free Acid in Solutions of Uranyl Sulfate. Transfer an aliquant of the solution of uranyl sulfate that contains not more than 200 mg of uranium to a 100-ml beaker. Add 10 ml of the solution of sodium fluoride; then dilute the sample to 40 ml with water. Adjust the rate of flow of the titrant to 6 to 8 ml per minute; then titrate the sample, by means of the automatic titrator, with a standardized solution of 0.1 N sodium hydroxide.

#### EXPERIMENTAL

##### The Effect of Sodium Fluoride and Other Complexing Agents on the Potential Change at the Sulfuric Acid End Point in the Presence of Uranium.

In order to illustrate the effect of sodium fluoride on the magnitude of the potential change at the end point of the titration of free acid, solutions that contained sulfuric acid in the presence of uranium were titrated with standard sodium hydroxide by means of the Dow titrator, equipped with saturated calomel and glass electrodes. The recorded titration curves of pH versus volume of titrant are presented in Figure I.

It was found that the potential change at the end point in the titration of the solutions that contain sodium fluoride is increased approximately five-fold over the potential change which occurs when fluoride is not present. The uranium that is present in the solution is complexed by the fluoride. Preliminary tests indicated that this potential change is sufficient to operate the cut-off mechanism of the automatic differential titrator.

An examination of other known complexing agents for uranium was undertaken to determine whether any was better than sodium fluoride, since the use of sodium fluoride to complex uranium has certain disadvantages. For example, it is necessary to standardize the sodium hydroxide titrant in the presence of sodium fluoride when the automatic differential titrator is used, and the precision of the method decreases somewhat in the presence of large amounts of uranium.

The applicability of some other complexing agents for uranium was tested by titrating solutions that contained 100 mg of uranium and 0.2 milliequivalents of sulfuric acid in the presence of one gram of one of the following compounds: sodium thiocyanate, ammonium thiocyanate, sodium tartrate, sodium oxalate, and ammonium fluoride. The solutions were titrated with sodium hydroxide by means of the Dow Precision titrator. Examination of the titration curves showed that none of the compounds was as effective as sodium fluoride in complexing uranium. The magnitude of the potential change at the end point was increased somewhat by sodium thiocyanate, but not as much as by sodium fluoride. The other complexing agents were without effect.

#### The Effect of Sodium Fluoride on the Titration of Sulfuric Acid.

Tests were conducted to ascertain the applicability of the Sargent-Malmstadt differential titrator to the determination of sulfuric acid in the presence of sodium fluoride. The cut-off point of the titration was established by titrating solutions of sulfuric acid with sodium hydroxide, in the presence and absence of fluoride ions, both, manually,

with a pH meter, and, automatically, with the differential titrator. The results are presented in Figure II. These results indicate that, in the titration of sulfuric acid in the absence of fluoride, the volume of titrant that is consumed to the cut-off point of the automatic titrator essentially coincides with the stoichiometric end point. On the other hand, when the titration was performed in the presence of fluoride, the flow of titrant was automatically terminated before the stoichiometric end point. As shown on the neutralization curve in Figure II, the flow of titrant is terminated on the lower portion of the curve, where  $\frac{\Delta \text{pH}}{\Delta V}$  increased gradually. In this case less titrant was added than required for the stoichiometric reaction.

The discrepancy between the cut-off points of the differential titrator, in the presence and absence of fluoride, can be attributed to the response of the instrument when titrating a weak or strong acid. The automatic termination of the titration is actuated by a rapid change in the pH of the system. In the case of a strong acid, such as sulfuric, the change of pH with volume of titrant,  $\frac{\Delta \text{pH}}{\Delta V}$ , does not exhibit a sharp rise until the equivalence point is reached. With a weak acid, the initial rise in pH before the equivalence point and the subsequent change in  $\frac{\Delta \text{pH}}{\Delta V}$  is sufficient to actuate the cut-off mechanism of the instrument prematurely. This situation is analagous to the titration error when an indicator such as methyl red (pK value 4-5) is used for a similar acid.

On the basis of these tests, in order to correct for the end point error without modifying the instrument, it is recommended that the sodium hydroxide titrant be standardized by titrating a solution of

sulfuric acid which contains a fixed quantity of fluoride ion. It was found experimentally that, in the presence of from 100 to 200 mg of fluoride, the estimation of the end point did not vary.

The Titration of Sulfuric Acid in the Presence of Sodium Fluoride and Varying Amounts of Uranium. The effect of the uranium concentration was studied by titrating solutions that contained a known amount of sulfuric acid and sodium fluoride and varying amounts of uranium. The results are presented in Table I.

Table I

Titration of Sulfuric Acid in Solutions of Uranyl Sulfate  
by Means of the Sargent-Malmstadt Titrator

Conditions

Electrodes, Pt-10 per cent Rh vs. saturated calomel	
Volume, ml	40
Titrant, sodium hydroxide, N	0.1072
Rate of flow of titrant, ml per minute, approximately	6
Fluoride, mg	150

Uranium mg	Determinations N	Sulfuric Acid, Milliequivalents		Coefficient of Variation Per Cent
		Added	Found, Average	
50	8	0.423	0.421	1.5
100	8	0.423	0.424	1.7
200	6	0.104	0.106	1.0
	6	0.208	0.206	1.2
	8	0.423	0.420	1.7
	6	1.036	1.041	0.8
500	6	0.126	0.099	3.0
	6	0.518	0.507	5.0

A quantitative titration of the free acid was realized in all of the tests. The coefficient of variation was about 2 per cent in the presence of up to 200 mg of uranium. In the presence of 500 mg of uranium, however, the method was less precise; therefore, for maximum precision, it is recommended that the uranium be limited to about 200 mg.

#### DISCUSSION

The addition of 150 mg of fluoride to the solution was sufficient to complex as much as 500 mg of uranium<sup>(7)</sup> and, at the same time, to convert as much as one milliequivalent of sulfuric acid to hydrofluoric acid by metathesis. A small excess of fluoride is desirable in order to insure that all of the free acid is present as HF since the sodium hydroxide titrant was standardized under the same conditions.

It should be pointed out that the possibility of attack on the glassware by the HF is notable. In dilute solutions which contained as much as one milliequivalent of acid in a volume of 40 ml, however, this reaction was not observed. In concentrated solutions, it would be necessary to take precautions. The use of the Sargent-Malmstadt differential titrator, under these conditions, is particularly advantageous. Since, with this instrument, a platinum or a platinum-10 per cent rhodium electrode can be used as a pH indicating electrode, it can be applied to the determination of the free acid content in solutions which attack the conventional, glass, pH-indicating electrode. The use of polyethylene beakers is recommended where large amounts of free acid are titrated in the presence of fluoride.

## ACKNOWLEDGEMENT

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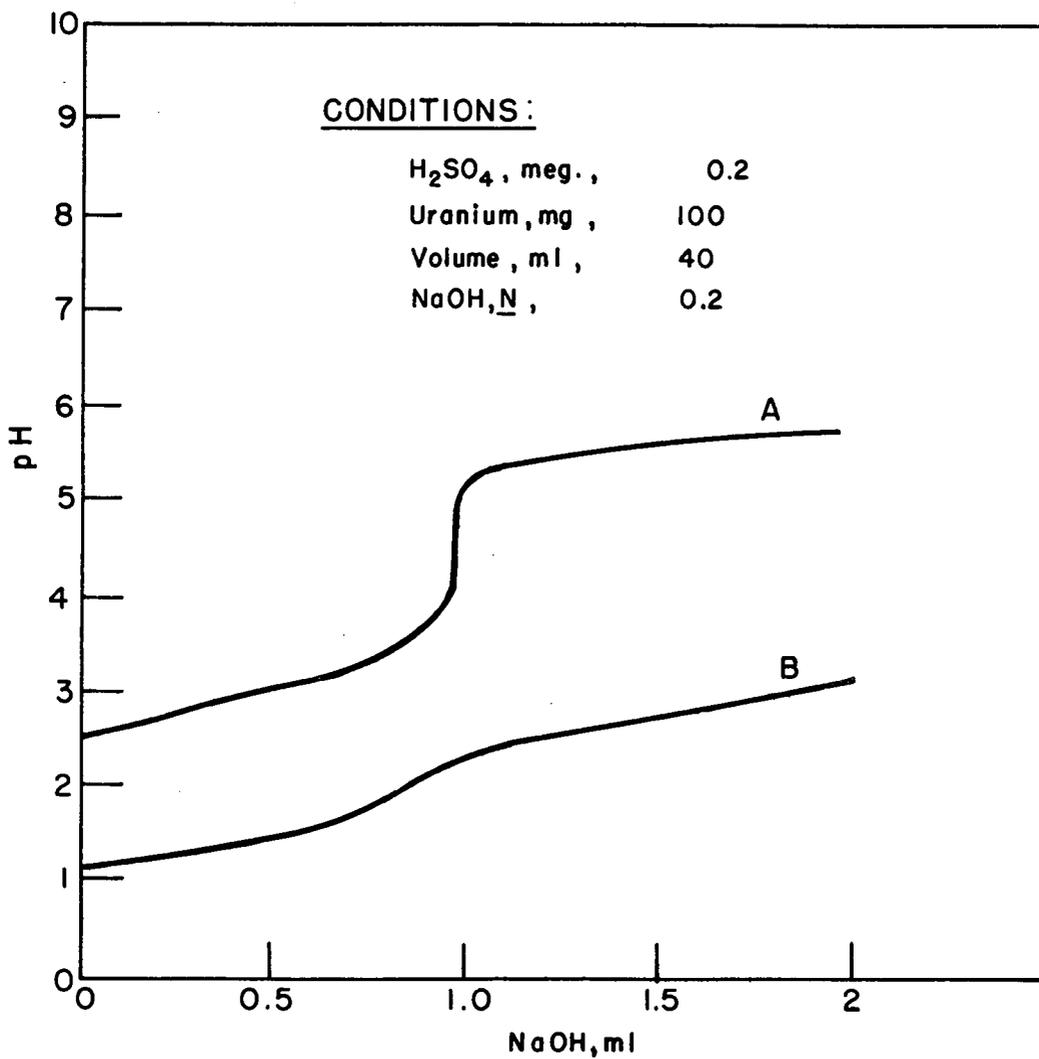
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A. 150 mg FLUORIDE PRESENT.  
B. FLUORIDE ABSENT.

FIGURE I. The Effect of Sodium Fluoride on the Magnitude of the Potential Change at the Free Acid End Point.

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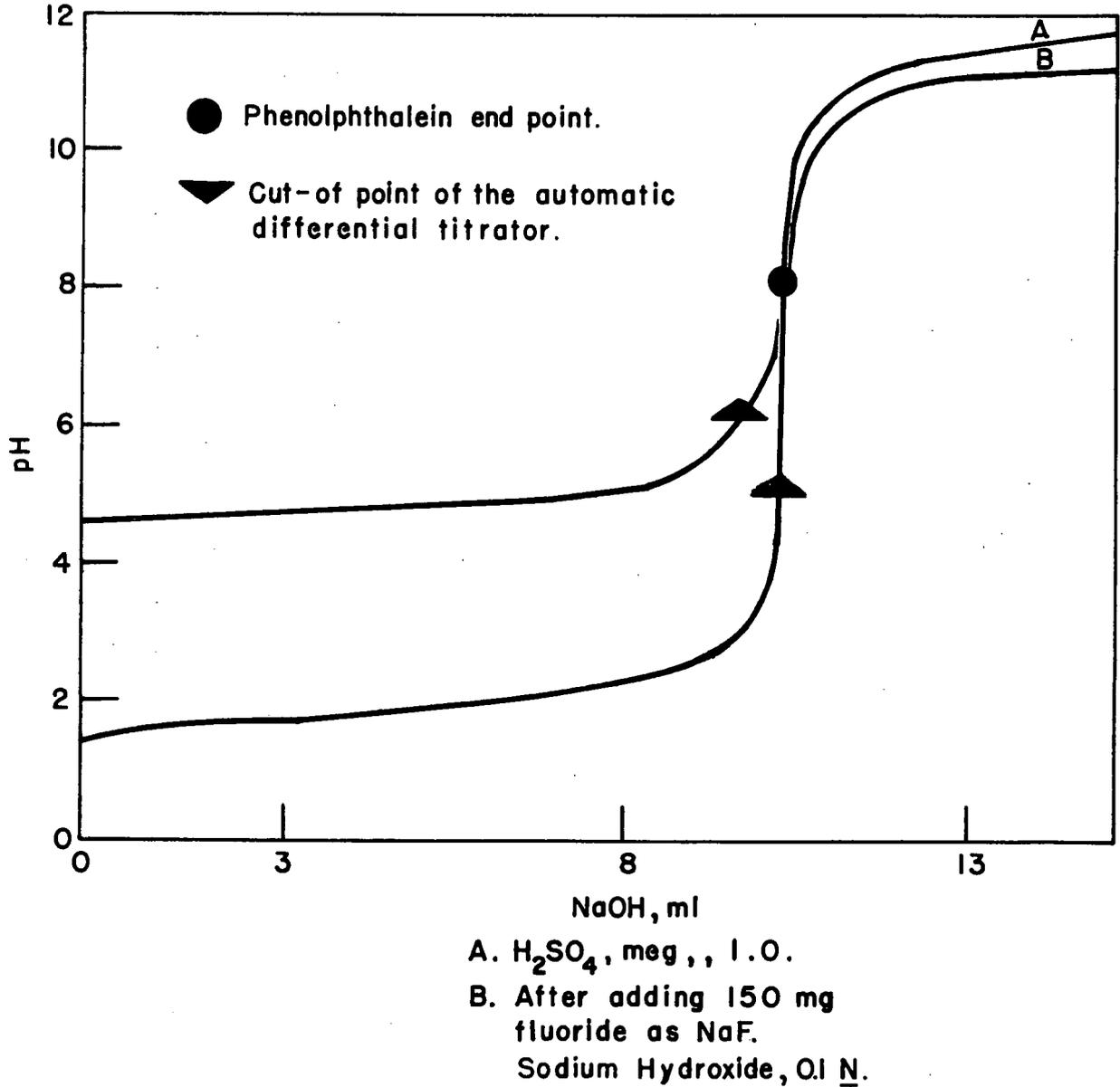


FIGURE 2. The Titration of Sulfuric Acid in the presence of Sodium Fluoride.