

# THE USE OF SEPARAN AS A MAXIMUM SUPPRESSOR IN POLAROGRAPHY

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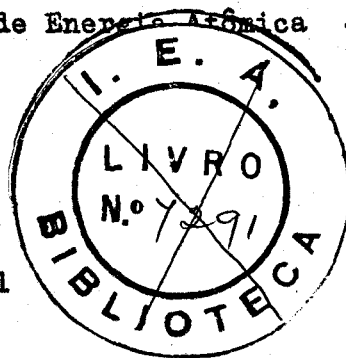
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Summary. The extensive use of separan as a maximum suppressor in Polarography is described. Like the very popular gelatin, separan can suppress the maxima of various metal ions over a wide range of potential, and it can be used in acid, alkaline (or ammoniacal) as well as in neutral media, having the additional advantage that the reagent is stable for a long time and does not decrease the diffusion current when applied in concentrations up to 1.0%. Measurements of U-VI in U-IV, of Zn, Pb, Cu and Te have been accomplished in the presence of separan.

Resumo. Neste trabalho descreve-se o uso de separan como um eficiente supressor de máxima e polarografia. Assim como a gelatina, muito usada neste campo, o separan pode suprimir ou eliminar o inconveniente fenômeno de máxima para vários ions metálicos num grande intervalo de potencial. Este suppressor pode ser usado em meio ácido, neutro ou alcalino, tendo a vantagem adicional de ser estável por muito tempo e não diminuir a corrente de difusão (como o faz a gelatina) quando aplicado em concentrações até 1,0%. Foram feitas medidas de U-VI em U-IV, de Zn, Pb, Cu e Te na presença de separan.

Resumé. Le but de ce travail est de décrire l'emploi du separan en polarographie, comme supresseur de maxima. Le separan, ainsi bien que la gélatine, peut être employé pour éliminer le phénomène des maxima dans le cas de plusieurs ions métalliques, dans un large intervalle de potentiel. Ce supresseur peut être employé dans des milieux acides, neutres ou alcalins avec l'avantage d'être stable pendant un temps assez long et de ne pas diminuer le courant de diffusion (comme c'est le cas de la gélatine), lorsqu'il est en des concentrations jusqu'à 1,0%. Déterminations de U-VI dans U-IV, de Zn, Pb, Cu et Te on été faites en présence de separan.

The Use of Separan as a Maximum Suppressor in Polarography.

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One of the general characteristics of the current-voltage curves (cv) with the dropping mercury electrode (d. e.) is the more or less pronounced maximum phenomenon, which is often observed unless special measures are taken to prevent its occurrence. The maxima observed with the d.e. are perfectly reproducible and the shapes of maxima vary from very acute peaks to rounded humps, depending on the composition of the solution.

The height of the maximum of a given electroreducible substance is greatly dependent on its concentration, and as a rule, there is no simple relation between the height of a maximum and the concentration of the reducible substance. The magnitudes of maxima depend on the time, becoming smaller the slower the drop time (1).

Heyrovsky (1) distinguishes between "positive" and "negative" maxima, according to whether a given maximum occurs, being the maximum in the electrocapillary curve about -0.6 volts against normal calomel in the absence of capillary active substances. For instance lead and thallos-ion shows positive maxima (at about -0.4 and -0.5 volts, respectively) and nickel shows a negative maxima (at about -1.1 volt).

Maxima can be suppressed or eliminated, by adding to the solution traces of certain capillary-active electrolytes

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and nonelectrolytes, and various non-capillary-active ions, and charged colloids.

Heyrovsky (2) states that acid dyes suppress the positive maximum, whereas basic dyes cause a suppression of negative maximum. For instance the positive maximum of thallium is suppressed by acid fuchsine (anion) but that of nickel is unaffected and on the other hand, basic fuchsine (cation) suppresses the negative nickel maximum.

The occurrence of maxima is a nuisance in practical analytical work, but they can be eliminated by the addition of suitable capillary-active ions. For example, positive maxima of thallium and lead in neutral solution are completely suppressed by traces of the sodium salt of the indicator methyl red. However, the positive lead maximum is not suppressed by the cation form of methyl red in acid medium, which is in accordance with Heyrovsky's rule (2). On the other hand, the negative maximum of nickel in neutral medium was found to be unaffected by the anion form of methyl red, but in acid medium the maximum was completely eliminated by the cation form of the dye, which is also in accord with Heyrovsky's rule.

Methyl red is itself reduced at the d.e., but the concentrations of the dye used to suppress maxima are so small (less than 0.001%) that they have no appreciable effect on the diffusion current of the substance to be determined.

In the absence of maxima suppressors no definite measure of the diffusion current can be obtained.

Capillary-active nonelectrolytes can also be very

effective in suppressing and eliminating maxima, but in general it is not to be expected that a certain capillary-active substance will be able to suppress maxima over the entire voltage range. Gelatin, for instance, even in very small concentration, is able to suppress the maxima of various ions over a wide range of potential (6). A concentration of gelatin of 0.02% is sufficient to suppress completely the lead maximum (3), but when its concentration is greater than about 0.01% it decreases the diffusion currents. Gelatin has been used to suppress maxima in acid, alkaline (or ammoniacal) as well as in neutral media. In practical work the suppressive effect of gelatin on the diffusion current, when it is present at concentrations greater than 0.01%, must be taken into account.

#### The use of separan.

In our laboratory we have extensively used separan as a suppressor of maxima. Separan NP-10 is a commercially available reagent manufactured by the Dow Chemical Company, Midland, Michigan, U.S.A.

Like the very popular gelatin, separan can suppress the maxima of various metal ions over a wide range of potential, it can be used in acid, alkaline (or ammoniacal), as well as in neutral media, having the additional advantage that the reagent is stable for a long time and does not decrease the diffusion current when applied in concentration about 0.8% in many examples which were studied in this paper, like U-IV and U-VI, Zn, Pb, Cu, and Te.

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## Experimental

### Apparatus.

During the work a Recording Polarograph, Model XXI, E. H. Sargent & Co., Chicago, U.S.A., was used. The original cell was substituted by one with adaptation for the saturated calomel electrode (SCE). The nitrogen gas was purified by bubbling in a Cr-III chloride solution maintained over a 2% liquid zinc amalgam, followed by a water washing. The  $m^{2/3} t^{1/6}$  constant is 1.69, this constant being determined at a constant applied potential of -0.5 volts x SCE in a 0.1 M KCl solution.

### Reagents.

1. Separan NP-10, The Dow Chemical Co., Midland, Michigan, USA.

A 1% aqueous solution was prepared by slow mechanical stirring of the powder added in small portions to 100 ml of deionized water. The solution was stored in a glass bottle and used throughout the work.

2. Uranium. Pellets of uranium dioxide were dissolved in a mixture of sulfuric-phosphoric acids to be analysed in respect to the U-VI contamination.  $UO_2$  pellets were manufactured by Divisão de Metalurgia Nuclear, Instituto de Energia Atômica, with nuclear grade ammonium diuranate (ADU) purified by the Pilot Plant of the Divisão de Radioquímica, Instituto de Energia Atômica, São Paulo.

Deionized water was used throughout this work and all reagents used were analytical C.P. grade.

I. Uranium Maxima.



For the determination of U-VI (uranyl ion) in highly pure uranium oxides, mainly in  $UO_2$  pellets, the oxide samples are dissolved in hot, concentrated phosphoric acid, and the uranium-VI is determined polarographically in a sulfuric-phosphoric acid medium with the dropping electrode. In our laboratory we have made use of the procedure of Burd and Goward (7) after introducing some modification.

To measure the diffusion current of U-VI in a phosphoric-sulfuric acid supporting electrolyte, the solution was purged with nitrogen and the polarogram recorded in the presence of methyl red as maximum suppressor; unexpectedly, a very pronounced maximum was registered.

Rodden (8) mentions the use of various maxima suppressors, including gelatin, methyl red, methyl cellulose, caffeine and thymol for the polarographic determination of uranium. As advised by the work of Burd and Goward (7), we started making use of methyl red as suppressor of maxima and at least, working with the uranium dioxide samples prepared in this Instituto, this suppressor was found to function unsatisfactorily.

Figure 1 shows typical polarograms of uranium-VI with methyl red (MR) and separan added as maximum suppressor, in 20 ml of a solution containing 0.25 g of  $UO_2$  and phosphoric-sulfuric acid as supporting electrolyte. Curve (1) corresponds to 0.0004% MR and no separan, curve (2) to 0.0004% MR plus 0.0004% separan, curve (3) 0.0004% MR plus 0.001% separan and curve (4) to 0.0004% MR and 0.0016% separan. On the last polarogram the maximum was completely suppressed and the current is diffusion controlled.

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Figure 2, curves (1), (2) and (3) are the polarograms recorded with a 20 g/l  $UO_2$  solution in a phosphoric-sulfuric acid supporting electrolyte, having 0.0004% MR, 0.002% MR and 0.001% of separan, respectively.

The same experiments were performed substituting methyl red by methyl orange, the latter being also unsatisfactory as a maximum suppressor for uranyl ion in sulfuric-phosphoric media.

## II. Copper maxima.

The uncontrolled diffusion current of cupric ions can be seen on figure 3, where the polarogram (1) was recorded without a maximum suppressor while polarograms (2) and (3), were recorded with 0.001% and 0.003% of separan, respectively. The supporting electrolyte was 1M  $NH_4OH$  plus 1M  $NH_4Cl$  and the concentration was 0.160 g/l in copper.

## III. Zinc maxima.

The effect of separan as a maximum suppressor is shown on figure 4, where the polarograms of zinc ions in a 1M  $NH_4OH$  plus 1M  $NH_4Cl$  media were recorded without suppressor (1), with 0.008% of separan (2), with 0.01% of methyl orange (3) and with 0.01% methyl red (4), respectively. The metal concentration in the four solutions was 0.272 g/l in zinc.

## IV. Lead maxima.

It is well known that gelatin in concentration of about 0.02% suppresses completely the lead maximum, but by increasing its concentration it decreases the diffusion current. So,

Uranyl wave in  $\text{UO}_2$  (12,500 g/l) in phosphoric-sulfuric acid.

- (1) 0.0004% methyl red (MR)
- (2) 0.0004% MR + 0.0004% separan
- (3) 0.0004% MR + 0.001% separan
- (4) 0.0004% MR + 0.0016% separan

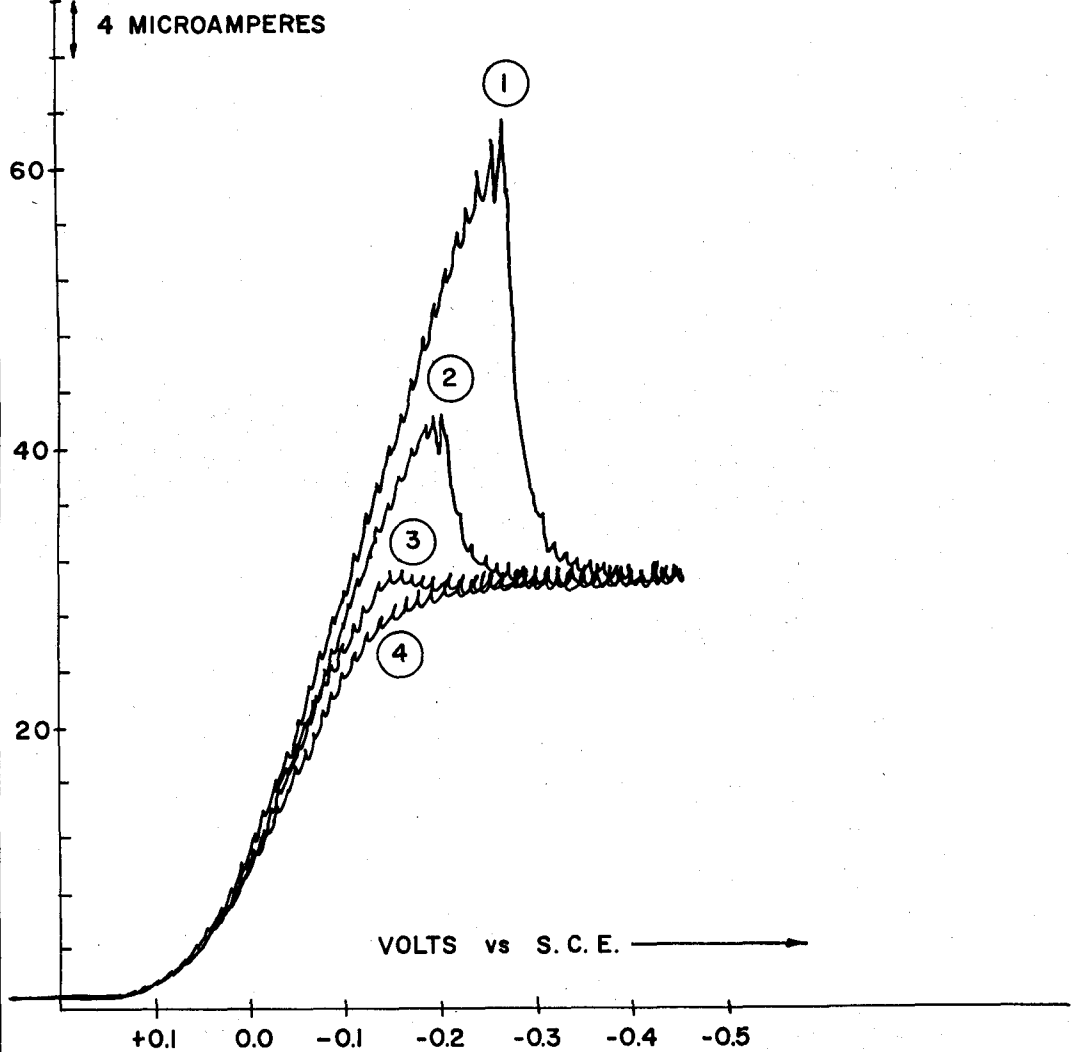


FIG. 1

Uranyl wave in  $\text{UO}_2$  (20. g/l) in phosphoric-sulfuric acid.

(1) 0.0004% methyl red

(2) 0.002% methyl red

(3) 0.001% separan

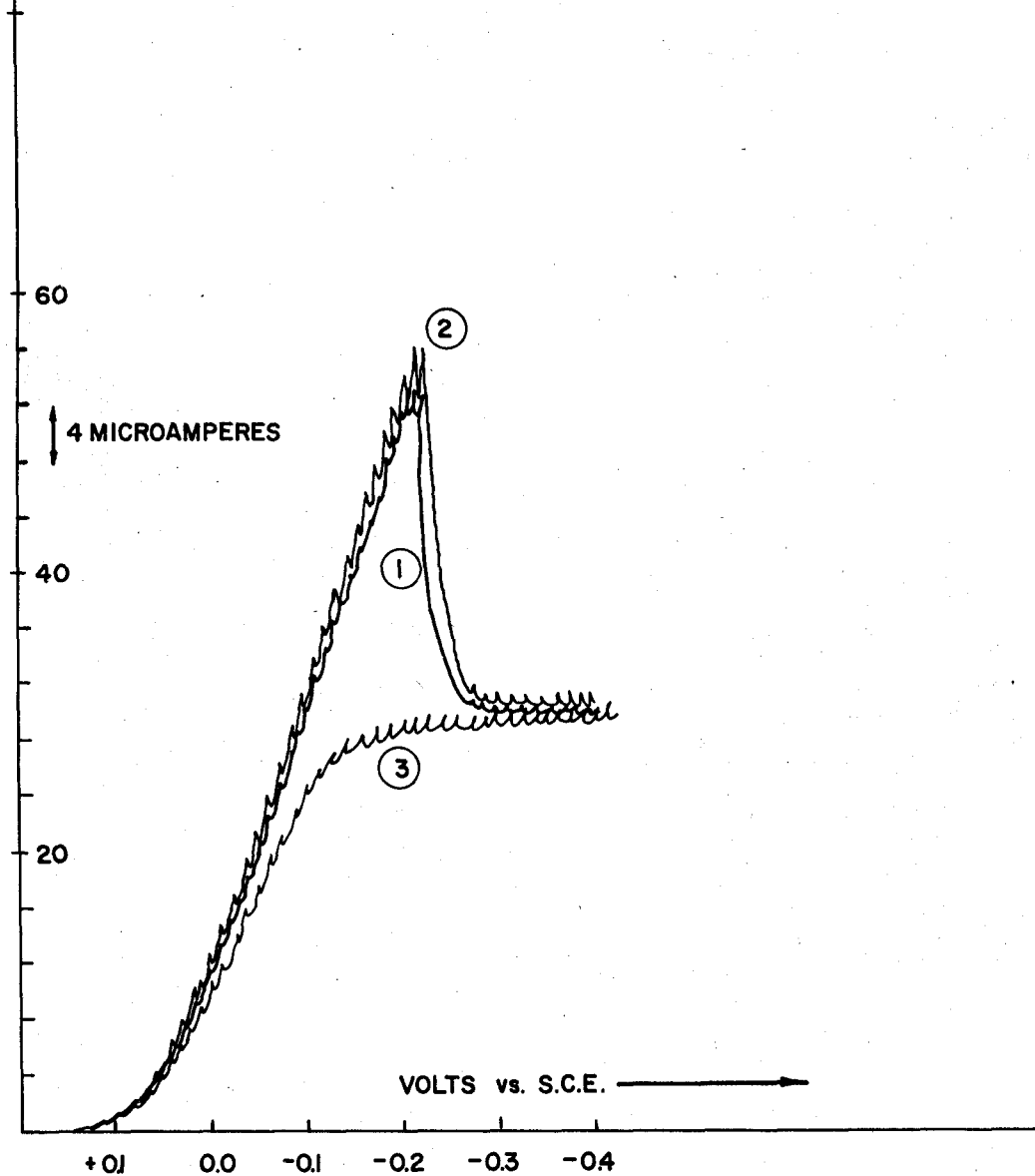


FIG. 2

0.160 g/l of copper in 1M  $\text{NH}_4\text{OH}$  + 1M  $\text{NH}_4\text{Cl}$

(1) without suppressor

(2) 0.001% of separan

(3) 0.003% of separan

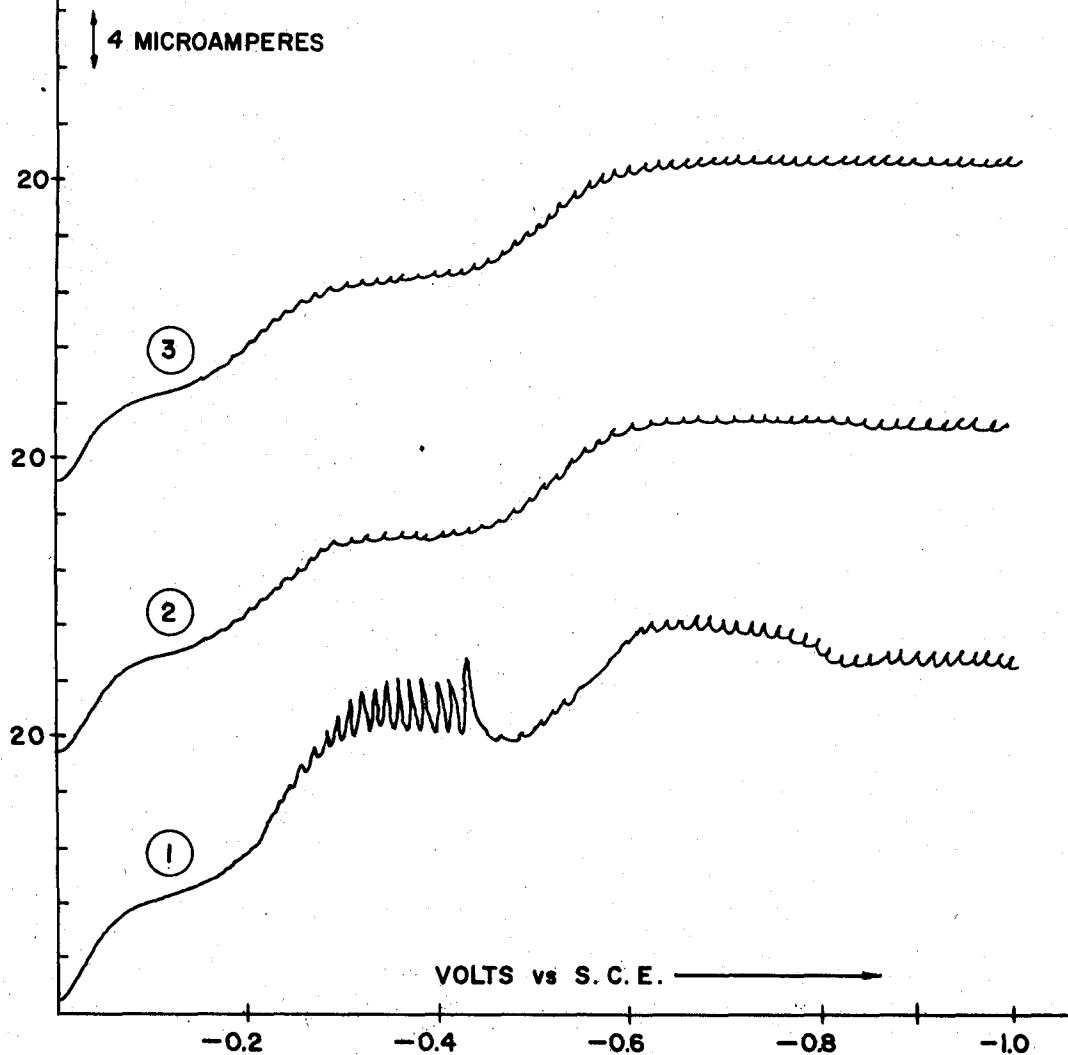


FIG. 3

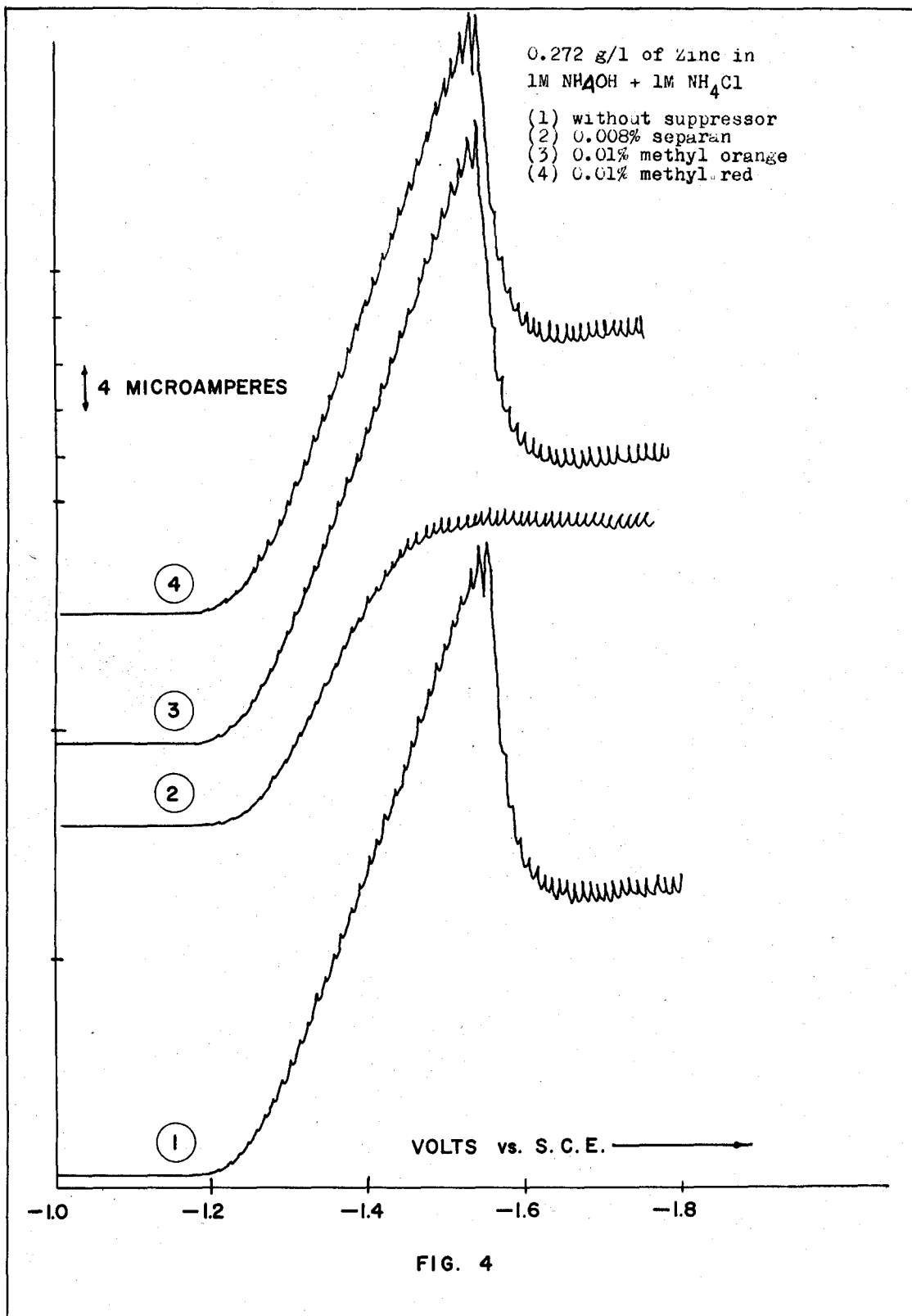


FIG. 4

in practical work the suppressive effect of gelatin on the diffusion current when present at concentrations greater than 0.01% must be taken into account. This situation is made very clear (3) with lead nitrate solutions in 0.1M potassium chloride and various concentrations of gelatin. For instance, 1% gelatin is enough to lower the diffusion current to about half of its height. At the same concentration separan suppresses the lead maximum without lowering the diffusion current. Figure 5 shows the uncontrolled diffusion current when the polarogram of lead (0.400 g/l in Pb) in a potassium chloride supporting electrolyte is recorded without a maximum suppressor (1), compared with the polarogram recorded after the addition of 0.02% of separan (2).

By increasing successively the concentration of separan we recorded a series of polarograms of lead nitrate (0.400 g/l in Pb) in 0.1M potassium chloride and conclude that separan does not lower the lead diffusion current (Table 1).

Table 1

Diffusion currents of lead in 0.1M KCl and  
separan as maximum suppressor

<u>Separan</u> <u>%</u>	<u>Diffusion Current</u> <u>(microampères)</u>
0.01	10.8
0.02	10.9
0.09	10.8
0.50	10.8
0.80	10.8
1.00	10.8

Figure 6 is the lead polarogram recorded without a maximum suppressor (A) and curve (B) is the same solution with 0.01% of separan. Both solutions were  $1.93 \times 10^{-3}M$  in lead and slightly acidified with nitric acid.

8.

A series of lead polarograms was recorded in the presence of separan as a maximum suppressor and with the same solutions were recorded new polarograms one month later. - This experiment allows to conclude that there was no alteration (Table 2) of the composition of the solutions and that separan is stable at least during one month in such a medium.

Table 2

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Diffusion currents of lead nitrate in slightly nitric acid medium, with separan as a maximum suppressor.

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Solution n.	Separan %	Diffusion Current (microampères)	
		1 <sup>st</sup> polarogram	2 <sup>nd</sup> polarogram one month later
1	0.001	11.0	10.9
2	0.02	11.3	11.6
3	0.10	11.3	11.2
4	0.80	11.2	10.9

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#### V. Tellurium.

Polarograms of tellurous acid (Te-IV) were recorded using separan as maximum suppressor. Tellurous acid and its ions undergo reduction at the d.e. showing a typical large maximum (4): The polarograms were recorded using solutions of  $1.10^{-3}$  M tellurous acid in a 1M  $\text{NH}_4\text{Cl}$  containing  $\text{NH}_4\text{OH}$  (pH 8.80) and separan as suppressor. There is no variation of diffusion current at high percentages of separan, as occurring with gelatin (5). It is reported that the very large maximum of  $\text{Te}^{4+}$  is unusual and exceptionally (5) indifferent to the usual maximum suppressors. Here again sepa-



0.400 g/l of Lead in KCl.

(1) without suppressor

(2) 0.02% of separan

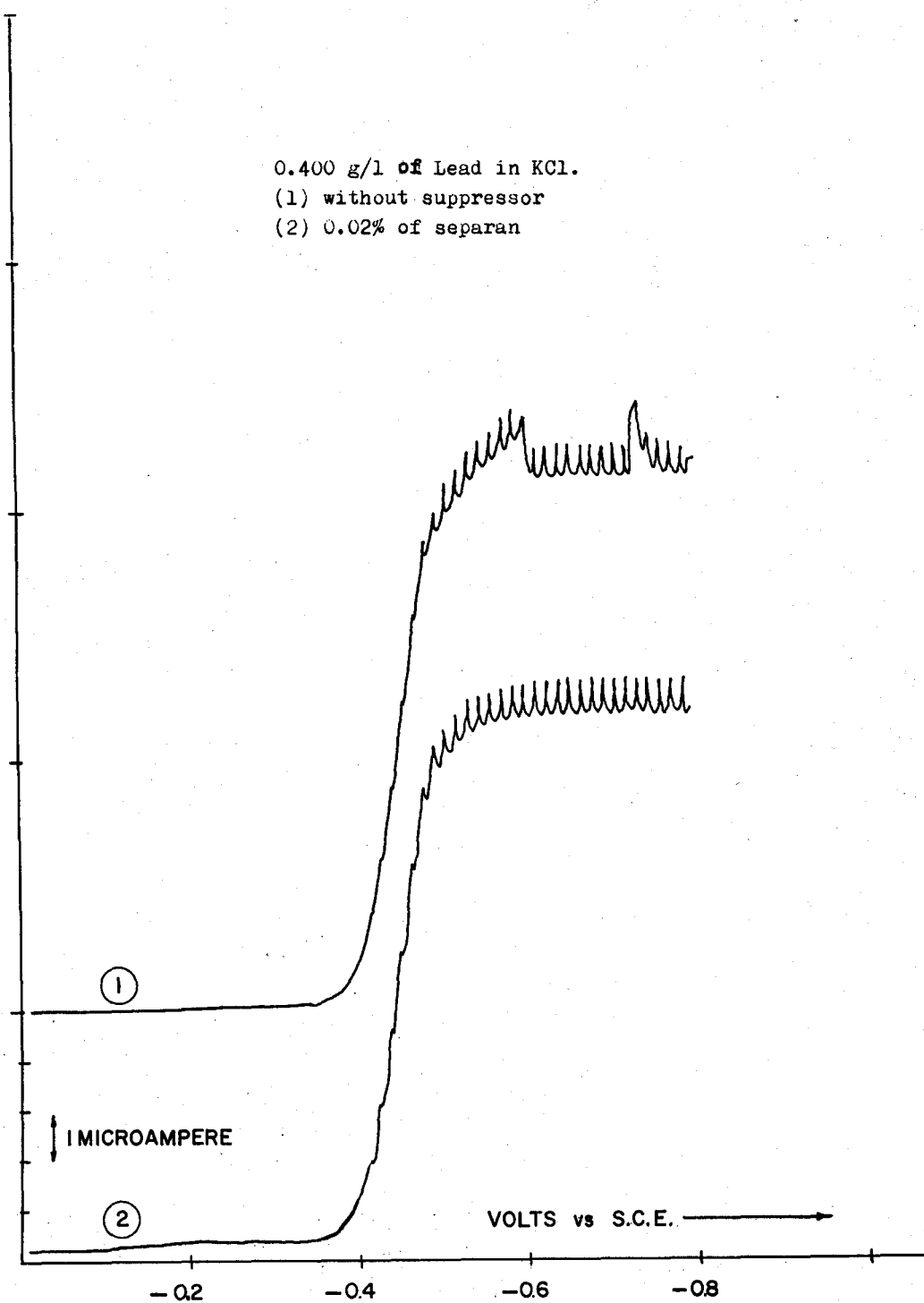


FIG. 5

$1.93 \times 10^{-3} \text{M}$  of Pb in  $\text{HNO}_3$ .

(A) without suppressor

(B) 0.01% of separan

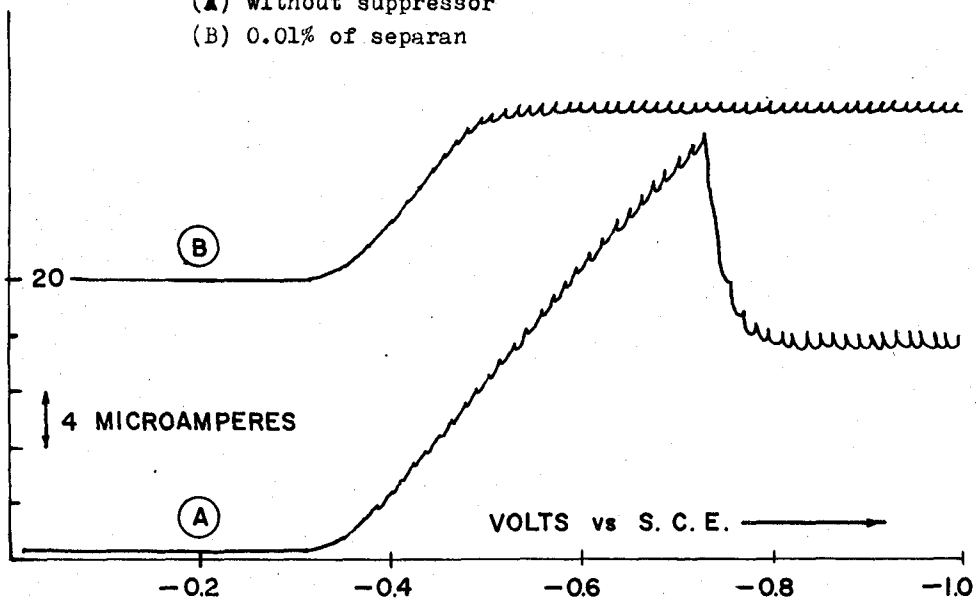


FIG. 6

1.10<sup>-3</sup>M Tellurous ion in 1M NH<sub>4</sub>Cl+ NH<sub>4</sub>OH, pH 8.80

- (1) without suppressor
- (2) 0.005% separan
- (3) 0.01% separan
- (4) 0.02% separan
- (5) 0.005% gelatin

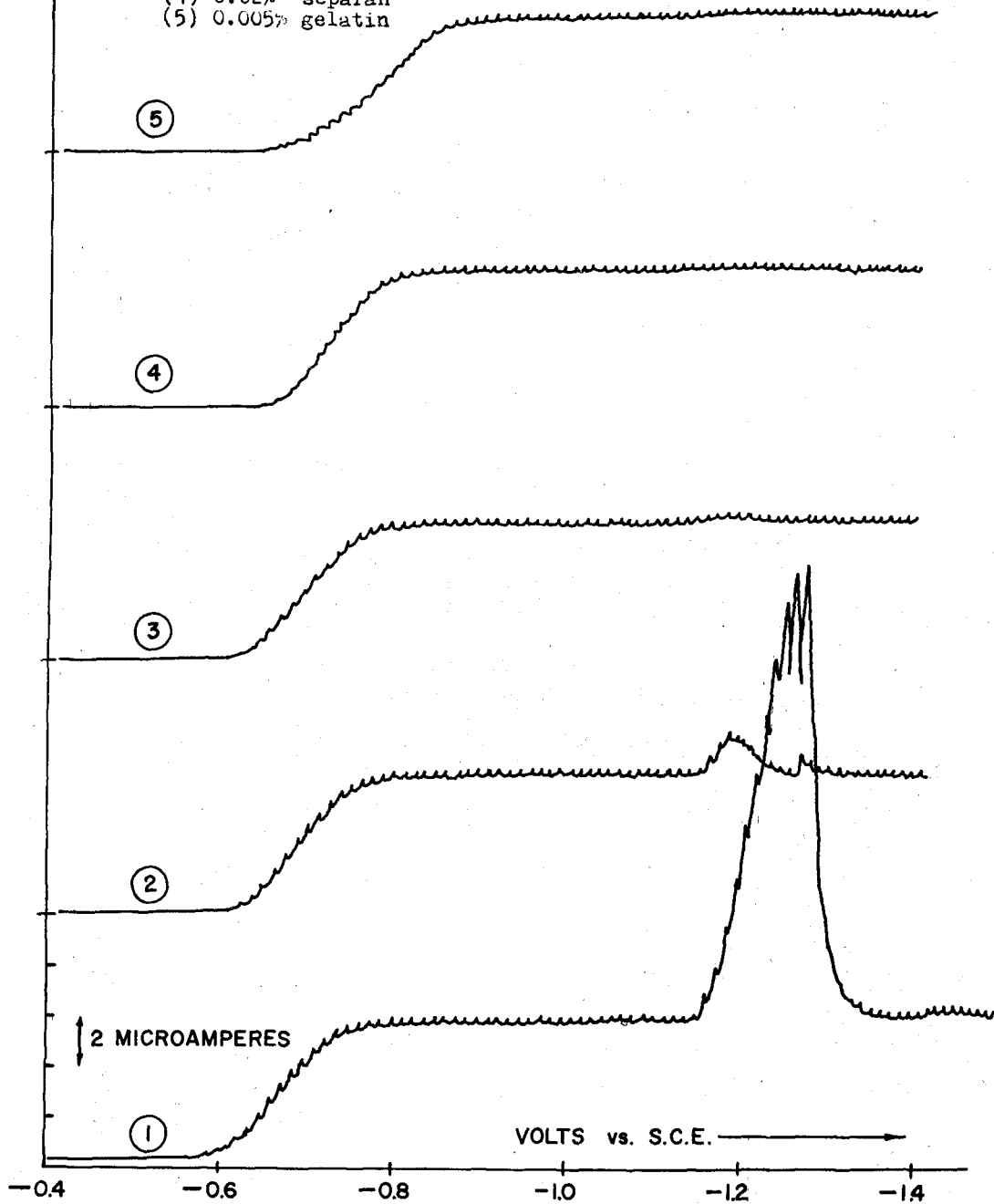


FIG. 7

ran is effective in suppressing this maximum.

Figure 7, curves (1) to (5) show polarograms of  $1.10^{-3}$ M tellurous ion in 1M ammonium chloride and ammonium hydroxide, at pH 8.80, having 0.0, 0.005, 0.01 and 0.02% of separan and 0.005% of gelatin, respectively.

### Conclusion.

It is shown that separan is an efficient maximum suppressor and can be applied in analytical polarographic work with many advantages:

1. it is used satisfactorily over a wide range of potentials;
2. it can be used in acid, alkaline (or ammoniacal) as well as in neutral media;
3. it is stable for a long time;
4. it does not decrease the diffusion current when applied in relatively large concentration (until 1.0%) as demonstrated in the case of lead and tellurous acid.

Specially for the uranium dioxide samples analysed in our laboratory for the U-VI (uranyl ion) content, in a sulfuric-phosphoric acid media, separan proved to be an efficient maximum suppressor. In this case methyl red, as suggested by the work of Burd and Goward (7) was completely unsatisfactory. Like in the case of the lead polarograms (2) where its positive maximum was suppressed by methyl red in neutral solutions but not suppressed in acid medium, the same dye does not suppress the positive maximum of uranyl ion in sulfuric-phosphoric acid medium.

10.

Acknowledgment.

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Literature cited.

- (1) I.M.Kolthoff and J.J.Lingane - Polarography; Interscience Publishers, Ltd., 2nd edition (1952), vol.1, pg. 160.
- (2) *ibid*, pg. 162.
- (3) *ibid*, pg. 164 and 165.
- (4) *ibid*, vol. 2, pg. 568.
- (5) *ibid*, vol. 2, pg. 570.
- (6) *ibid*, vol. 1, pg. 164.
- (7) R.M. Burd and G.W.Goward. The Polarographic Determination of Hexavalent Uranium in Uranium Oxides: the Determination of Oxygen-Uranium Ratios. April, 1959, WAPD-205, AEC Research and Development Report - Contract AT-11-1-GEN-14. Bettis Plant, Pittsburgh, Pa., USA.
- (8) C.J. Rodden - Analytical Chemistry of the Manhattan Project, New York, McGraw Hill, 1950, pg. 605.