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TECHNICAL REPORT NO. 3

DETERMINATION OF SULFIDE
BY CATHODIC STRIPPING
VOLTAMMETRY AT A ROTATING
SILVER DISC ELECTRODE

by

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Accepted for Publication in
Analytical Chemistry

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Abstract

→ The deposition and stripping behavior of silver sulfide films at the silver rotating disc electrode were investigated. The effect of various factors - rotation rate, scan rate, deposition potential and time, and concentration of sulfide ion - on the stripping peak current and potential were studied. The electrode has been found to be an excellent electrode for cathodic stripping voltammetry for the determination of submicro amount of sulfide ion. Furthermore, differential pulse voltammetry significantly enhanced the signal/noise ratio, and a linear response was obtained over the concentration range $(10^{-8} - 10^{-5})$ mol / cu dm³ of sulfide ion in 0.2 mol / cu dm³ NaOH.

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A

We wish to describe a procedure for trace determination of sulfide ion in solution based upon the cathodic stripping of electrodeposited Ag_2S . This procedure evolved from studies of the formation of silver sulfide upon anodization of a silver electrode in sulfide containing solutions and the properties of the electrodeposited silver sulfide films at silver rotating disc electrodes (RDE) (1,2).

Although anodic stripping voltammetry (ASV) is a well established technique for the determination of trace levels of metal ions in solution, the equivalent method for the determination of anions by cathodic stripping voltammetry (CSV) is less established. Most of the reported application of CSV for anions which form sparingly soluble compounds with the electrode have been carried out at hanging mercury drop or mercury pool electrodes. The determination of trace quantities of halide (3 - 5), sulfide (6 - 11), cyanide (12), cyanoferrate (II) and (III) (13) and selenide ions (14 - 15), and various thiols (16 - 21) by deposition of their insoluble mercury salts has been reported. Several extensive reviews (22 - 24) covering stripping analysis have appeared and the reviews by Brainina have extensive sections on CSV.

Trace amounts of iodide were determined by CSV by Shain and Perone (25) as early as 1961. Although they used a silver electrode, it appears that little work with this electrode for CSV has been performed since.

To increase the efficiency of the deposition step, the solution containing the analyte is usually vigorously stirred during deposition (ASV) or film formation (CSV). The stripping (ASV) step is usually carried out from a quiescent solution since stirring perturbs the

mercury drop or pool electrode (26). Since the rotating electrode hydrodynamics are very well defined, increasing use has been made of thin-film mercury electrodes on rotating glassy carbon substrates. However, there is a significant lack of literature on the use of an RDE for anion determinations employing CSV.

This paper reports on the deposition and stripping of silver sulfide films at a silver RDE and describes a procedure for the determination of submicro levels of sulfide. Linear potential scan or differential pulse voltammetry is employed during the reduction step stripping the Ag_2S from the electrode surface.

EXPERIMENTAL

Reagents

Analytical grade sodium sulfide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, Mallinckrodt Inc.) and sodium hydroxide (Fisher Scientific Co. reagent grade or ultrapure, $\text{NaOH}\cdot\text{H}_2\text{O}$, Alfa Products), were used.

Solutions were prepared with water purified using a Milli -Q Purification system. Standardization of sodium sulfide in a stock solution approximately 0.6 mol dm^{-3} in 1.0 mol dm^{-3} NaOH was performed iodometrically (22,23). Calibration curves were prepared by plotting the anodic limiting current for silver sulfide deposition vs the concentration of sodium sulfide; a silver RDE rotating at 2500 rpm was employed. The concentration of sodium sulfide in the stock solution was occasionally redetermined employing the calibration curve.

Apparatus

The silver disk electrode, electrode assembly, electrolysis cell, and the rotator used in this study will be described elsewhere (1), but are essentially of standard configuration. The geometrical area of the electrode surface was 0.462 cm^2 .

A Stripping Voltammeter, model EC 220 (IBM Instrument Systems) was employed for the constant potential electrolysis, linear potential scan and differential pulse voltammetry. An Omnigraph Model 2000 XY - Recorder (Houston Instrument Co.) was used to record the voltammograms.

The cell was thermostatted and all experiments run at (25 ± 0.2) °C. Potentials are reported with respect to a saturated calomel electrode (SCE).

Experimental Procedure

The electrode surface was polished prior to immersion in the electrolytic solution with 0.3 μm alumina (Dry Powder, Type A, Fisher Scientific Co.) on a polishing cloth (Fisher polishing cloth, 12 - 28, 2B). Polishing was not necessary before each measurement and ten or more experiments without polishing gave highly reproducible stripping voltammograms.

The solution to be analyzed was deaerated by bubbling with argon passed through acidic vanadium (II) solution and water. The sodium sulfide solution was added to the background solution with a 5×10^{-5} dm^3 Eppendorff pipet.

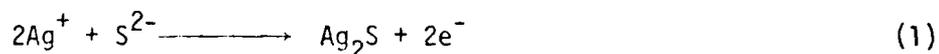
The electrode surface was first conditioned at a constant potential of - 1.20 V with rotation until a constant current ($\sim 10 \mu\text{A}$) was obtained. The potential was then stepped to the deposition potential; the electrode was rotated during the deposition of the silver sulfide. The deposition time was controlled with an electrical timer within the voltammeter. During the deposition and stripping processes the solution was covered by an argon purge. The deposition potential was - 0.4 V in all experiments unless otherwise stated.

The deposited films were cathodically stripped by means of linear potential scan or differential pulse voltammetry; in some experiments the silver electrode was rotated during stripping. Cathodic stripping was initiated from the deposition potential without a rest time. The area under the peak for the linear potential scan, which is proportional to the quantity of electricity consumed during the stripping step, was determined by weighing the recorder paper or by a planimeter.

RESULTS AND DISCUSSION

Preliminary Observation

Fig. 1 shows a typical RDE voltammogram for sulfide ion in 0.2 mol dm⁻³ sodium hydroxide solution at a silver RDE. The major features are an oxidation step ($E_{1/2} = -0.71$ V) corresponding to the process



as described previously (2), and a sharp single reduction peak ($E_p = -0.91$ V) for the reverse process during the cathodic scan. The limiting current for the oxidation wave shown is convective diffusion controlled in sulfide ions (1).

Prior results indicated that the behavior of the limiting current at the silver RDE 1) is convection diffusion controlled, as indicated by adherence to the Levich equation and 2) is constant for a given period of time followed by the onset of a decrease in the RDE limiting current. The anodic limiting current during the period of current invariance is proportional to the concentration of sulfide in solution. The point at which the current starts to decrease depends on the quantity of electricity passed, hence the amount of silver sulfide deposited on the electrode surface (1,2). Thus, provided that the total quantity of electricity passed is kept less than this critical amount, Q_T , the deposition process is well defined, and the amount of silver sulfide deposited depends on the sulfide concentration, time of deposition, and rotation rate of the electrode. The detailed behavior alluded to here is described elsewhere (1). All work reported here corresponds to amounts of silver sulfide

deposited such that Q_a , the quantity of electricity passed during anodic deposition, was less than Q_r .

We have previously shown (1) that the quantity of electricity required to form Ag_2S (Q_a) is the same as that for the cathodic stripping of silver sulfide (Q_c), i.e.,

$$Q_a = Q_c \quad (2)$$

The results indicate 1) anodically deposited silver sulfide at silver electrodes does not dissolve chemically, 2) is not removed mechanically during deposition and 3) deposits are completely stripped during the cathodic scan. Hence, it is possible to determine the Q_a value that can not be directly determined experimentally at low concentrations of sulfide ion from the Q_c value obtained during the cathodic stripping process.

The potential at which the Ag_2S forms at the RDE is dependent on the concentration of sulfide in solution, shifting anodically as the concentration of sulfide decreases (2). Since the curves are not reversible, depending on the kinetics and mechanism of film formation, the optimum deposition potential was experimentally determined. Figure 2 shows the peak current obtained during a linear potential scan stripping voltammogram for a $3.0 \times 10^{-7} \text{ mol dm}^{-3}$ sulfide solution as a function of electrode potential during the film formation step. Based on this, a potential of -0.4 V was employed for Ag_2S deposition. In effect, this corresponds to a potential well onto the diffusion plateau of the sulfide wave (see Figure 1) at the lowest concentration of sulfide employed.

Anodic deposition step

By selecting the deposition potential at the limiting current region (- 0.4 V), the anodic current during film formation should follow the Levich equation. Thus, the quantity of electricity required for the formation of silver sulfide films during anodic depolarization of the silver electrode by sulfide ion is given as:

$$Q_a = I_d t_d \quad (3)$$

where

$$I_d = 6.2 \times 10^{-4} n F A D^{2/3} \nu^{-1/6} \omega^{1/2} c_s \quad (4)$$

I_d is the limiting current for anodic dissolution of the silver RDE in the presence of sulfide, c_s is the analytical concentration of sulfide in mol dm⁻³, t_d is the deposition time, and other variables have their usual meaning. From eqns. (2), (3) and (4), the quantity of electricity resulting from a cathodic scan should be directly proportional to c_s , t_d , and $\omega^{1/2}$.

Typical stripping voltammograms for the reduction of Ag₂S films formed from sulfide concentrations in the range 10⁻⁶ - 10⁻⁷ mol dm⁻³ are shown in Figure 3. Plots of the quantity of electricity under the stripping voltammograms, Q_c , against the concentration of sulfide, c_s , were linear, with a slight difference in slope depending on the scan rate employed. This is a result of the time spent, once the cathodic scan is initiated, at potentials where Ag₂S still forms on the electrode surface. Q_c is proportional to the concentration of sulfide in solution, and linearity at the scan rates employed (20-50 mV s⁻¹) is excellent. The Q_c - c_s plot, however, does not pass thru the origin, but has an

intercept on the c_s axis. This could be the result of trace heavy metal impurity or an inability to remove some of the Ag_2S . However, the former explanation is preferred, since use of "ultrapure" sodium hydroxide considerably decreased this "blank".

As expected, Q_c was linear with deposition time. At 3.0 and $6.0 \times 10^{-7} \text{ mol dm}^{-3}$ of sodium sulfide, the slopes of the $t_d - Q_c$ plots were $5.85 \times 10^{-7} \text{ A}$ and $1.24 \times 10^{-7} \text{ A}$, respectively, for a rotation rate of 2500 rpm, a deposition potential of -0.4 V , and a scan rate of 50 mV s^{-1} .

The effect of rotation rate on Q_c at $9.45 \times 10^{-7} \text{ mol dm}^{-3}$ of sulfide ion was also examined. A plot of $Q_c - \omega^{1/2} t_d$ was linear over the range of 400 rpm to 4900 rpm as expected from eqn. (3) and (4) with a slope of $1.03 \times 10^{-7} \text{ A s}^{1/2}$. The mean diffusion coefficient, \bar{D} , for HS^- and S^{2-} obtained from the slopes of $Q_c - \omega^{1/2} t_d$ plots and eqn. (3) was $2.79 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The value is in good agreement with a value of $2.64 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ obtained from the diffusion limited current of sulfide deposition at the silver RDE. It is clear that even in such dilute solution of sulfide ion the Levich equation is obeyed at the deposition potential of -0.4 V .

Cathodic stripping step

Brainina (23) has given a theoretical treatment for the particular case of irreversible cathodic film dissolution of the type $MA_n + ne^- \rightarrow M + nA^-$ in which the anion (A^-) has a single charge, but no theoretical treatment has been given for $M_nA + ne^- \rightarrow nM + A^{n-}$ such as the silver sulfide system. Hence, we examined experimentally the effect of Q_c and scan rate (v) on peak current (I_p) and peak potential (E_p).

Linear scan stripping voltammograms from a stationary or rotating (400-3600 rpm) electrode on which had been deposited the same amount of silver sulfide film were identical. This suggests that the cathodic stripping process of the silver sulfide film is not controlled by diffusion of sulfide ions from the electrode surface to the bulk but by other kinetics, and that the overall process for the stripping is irreversible. Electrode rotation should exert no effect on peak current in the case of irreversible systems. This behavior has also proposed as a diagnostic test of the reversibility of the electrooxidation of metal films from the surface of inert electrodes (29).

a) Peak current

The relationship between I_p and Q_c was examined by varying c_s for fixed values of t_d and ω during the film-formation step and for given values of v during the linear scan stripping step. I_p was directly proportional to Q_c up to ca $10^{-3}C$ and then gradually deviated from linearity. The values of the slopes at v of 50 mV s^{-1} and 20 mV s^{-1} were tabulated in Table I.

Fig. 4 shows the linear relationship between I_p and v for various amounts of Ag_2S deposited. Data for curves a and c in Fig. 4 were obtained by changing t_d at constant c_s , while that for b and d were obtained by changing c_s at a fixed t_d .

The experimental results indicated that I_p was directly proportional to Q_a and to v ; values of the proportionality constant are tabulated in Table 1 and lead to the following empirical expression,

$$(I_p/A) = -13.7 (Q_c/C)(v/V \text{ s}^{-1}) \quad (5)$$

While a theoretical basis for this equation has not been formulated, the similarity to that for thin layer electrochemistry cannot be ignored. For linear scan ASV it has been shown that a similar relationship with a proportionality constant of 11.7 V^{-1} is valid (30,31).

b) Peak potential

The effect of Q_c and v on the peak potential was also examined. At a given scan rate, the peak potential depends linearly on the logarithm of the quantity of electricity, which is proportional to the amount of deposit on the electrode (see Figure 3). Even under various deposition conditions chosen by changing t_d , ω , and c_s , the relationship above is still valid. Thus, the peak potential depends on t_d , ω and c_s only through Q_a .

The peak potential of the stripping peak was also linearly dependent on the log of the scan rate, v , at fixed Q_c .

The peak potential could be related to Q_c and v by the following empirical relation,

$$E_p = a \ln(Q_c/C) + b \ln(v/V \text{ s}^{-1}) + c \quad (6)$$

where a , b and c are constants which were obtained experimentally as 0.028 V, 0.027 V and 1.026 V respectively. It appears that the constants a and b are identical only that $E_p = k \ln(Q_c v/A V) + k'$.

Analytical application

a) Linear potential scan mode

The effects of various parameters described above demonstrate that cathodic stripping voltammetry at the silver RDE may be used for the determination of trace amounts of sulfide ion. It is highly desirable

for a stripping determination that the peak current be directly proportional to the concentration of the sulfide, which requires the deposition of a suitable amount of silver sulfide on the electrode. Widely varying concentrations of sulfide may be determined by changing the deposition time and rotation rate since the linear relationship between peak current and sulfide ion concentration can only be obtained in a certain region corresponding to a given amount of silver sulfide (quantity of electricity) at a given electrode surface area. Increasing Q_c to more than ca. 10^{-3} C results in the peak current deviating from linearity. By decreasing t_d or ω to a region where Q_c is proportional to I_p , a linear dependence should be obtained. However, for very small values of Q_c there may also be nonlinearity of Q_c on I_p because of the difference in activity of the deposited films due to a decrease in film thickness. In fact, I_p deviated slightly from linearity when Q_c was smaller than ca. 10^{-4} C.

Experimentally, it appears that the optimum value of Q_c per unit electrode surface area is from 2×10^{-4} C cm⁻² to 2×10^{-3} C cm⁻². Even if the deposition is carried out under different experimental conditions of deposition time or rotation rate, we were able to use a normalized calibration curve of $I_p / (t_d \omega^{1/2})$ vs c_s . Thus, it is possible to determine a wide range of sulfide ion concentrations by choosing suitable deposition times and rotation rates. In some instances, it is both useful and necessary to identify and quantitate an anion from a combination of experimental and theoretical results, rather than employing a calibration curve. The use of the silver RDE for sulfide analysis permits such a procedure. Comparison of sulfide ion concentrations

experimentally determined and those calculated from employing the linearity demonstrated between \underline{Q}_c and the various deposition parameters (eqns. (2), (3) and (4)), using a value of \underline{D} of $2.64 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, were tabulated in Table II.

The effect of peak current on scan rate suggests that increasing the scan rate has little advantage because both signal and noise in the stripping voltammogram are directly proportional to the scan rate. Scan rates of $20 \text{ mV s}^{-1} - 50 \text{ mV s}^{-1}$ are recommended.

b) Differential pulse mode

In order to increase the sensitivity by suppression of the residual current, a differential pulse technique was used as a monitor of cathodic stripping. Fig. 5 shows typical differential pulse stripping voltammograms in the range of $(10^{-6} - 10^{-7}) \text{ mol dm}^{-3}$ of Na_2S . For concentration of Na_2S less than $10^{-7} \text{ mol dm}^{-3}$ ultrapure sodium hydroxide ($\text{NaOH} \cdot \text{H}_2\text{O}$) was used as the supporting electrolyte. The peak current obtained in the differential pulse mode was directly proportional to \underline{c}_s when suitable values of \underline{Q}_c were chosen. Increasing \underline{Q}_c beyond a certain value (ca. $5 \times 10^{-4} \text{ C}$) resulted in the differential pulse peak current vs \underline{c}_s plot deviating from linearity (Table III). This deviation took place at lower \underline{Q}_c values for differential pulse stripping than for linear potential scan stripping. If the rotation of the electrode during the stripping step is stopped, the differential pulse mode peak current increased in contrast to the independence of the peak current with rotation rate in linear scan stripping. The residual current in the differential pulse mode also increased for stripping at a stationary electrode compared to the rotating electrode. Thus cessation of

electrode rotation does not enhance the sensitivity for analysis (Table IV).

The detection limits by linear potential scan and differential pulse stripping for sulfide ion under the same deposition conditions are compared in Table IV. From the results, it is clear that differential pulse stripping enhances the analytical sensitivity for sulfide ion about three times compared to linear potential scan stripping.

The application of a silver RDE in CSV permits sulfide to be determined in the range of $(10^{-8}-10^{-5})$ mol dm⁻³. The determination of other anions which form sparingly soluble compounds with silver ion should be possible at the silver RDE.

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Credit

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Figure Captions

Fig. 1. A typical cyclic voltammogram for sulfide ion at the silver RDE

Solution: $8.52 \times 10^{-5} \text{ mol dm}^{-3}$ of Na_2S in 0.20 mol dm^{-3} of NaOH , $\omega = 2500 \text{ rpm}$, $\nu = 25 \text{ mV s}^{-1}$, the potential was scanned from -1.20 V positive.

Fig. 2. Effect of deposition potential on peak current of cathodic stripping voltammogram

Solution: $3.0 \times 10^{-7} \text{ mol dm}^{-3}$ of Na_2S in 0.20 mol dm^{-3} of NaOH , $t_d = 620 \text{ s}$, $\omega = 2500 \text{ rpm}$, $\nu = 50 \text{ mV s}^{-1}$.

Fig. 3. Cathodic stripping voltammograms for sulfide ion with silver RDE

Concentration of Na_2S : (a) 1.0, (b) 2.0, (c) 3.0, (d) 4.0, (e) 5.0, (f) 6.0, (g) 7.0, (h) 8.0, (i) 9.0, (j) 10.0, (k) $0 \times 10^{-7} \text{ mol dm}^{-3}$ in 0.2 mol dm^{-3} of NaOH . $E_d = -0.40 \text{ V}$, $t_d = 620 \text{ s}$, $\omega = 2500 \text{ rpm}$, $\nu = 50 \text{ mV s}^{-1}$.

Fig. 4. Dependence of peak current on scan rate

Solutions: (■) and (□) 10^{-6} , (●) 1.2×10^{-6} , (○) $0.6 \times 10^{-6} \text{ mol dm}^{-3}$ of Na_2S in 0.20 mol dm^{-3} of NaOH .

$E_d = -0.40 \text{ V}$, t_d ; (■) 260 s, (□), (●) and (○) 140 s, $\omega = 2500 \text{ rpm}$.

Fig. 5. Typical differential stripping voltammograms for sulfide ion with silver RDE

Concentration of Na_2S : (a) 1.0, (b) 2.0, (c) 3.0, (d) 4.0, (e) 5.0, (f) 6.0, (g) 7.0, (h) 8.0, (i) 9.0, (j) 10.0, (k) $0 \times 10^{-7} \text{ mol dm}^{-3}$ in $0.2 \text{ mol dm}^{-3} \text{ NaOH}$.

$E_d = -0.40 \text{ V}$, $t_d = 620 \text{ s}$, $\omega = 2500 \text{ rpm}$, $v = 10 \text{ mV s}^{-1}$,
repetition rate = 0.4 s , pulse height = 40 mV , pulse width =
 50 ms , pulse delay = 33.3 ms , sampling time = 16.6 ms .

Table I. The experimental constant of Eqn. (5)

$-(I_p / Q_c) / s^{-1}$	$v / \text{mV } s^{-1}$	$-(I_p / Q_c v) / v^{-1}$
0.270±0.011	20	13.5
0.690±0.008	50	13.8
$-(I_p / v) / (10^{-3} \text{ C} / \text{V})$	$Q_c / 10^{-4} \text{ C}$	
1.90±0.03	1.40	13.6
4.00±0.07	2.95	13.6
2.95±0.09	2.20	13.5
5.75±0.10	4.09	14.1
		av. 13.7±0.2

The values of a) and b) were obtained from the slopes of experiments reported in the text ($c_s = (10^{-6} - 10^{-7}) \text{ mol dm}^{-3}$, $t_d = 620 \text{ S}$, $\omega = 2500 \text{ rpm}$) and (c), d), e) and f) were obtained from the slopes of data presented in Fig. 4.

Table II. Comparison of analytical concentration $(c_s)_a$ with that calculated $(c_s)_c$ from Q_c .

$(c_s)_a/10^{-7}$ mol dm ⁻³	$Q_c/10^{-4}$ C	$t_d/10^2$ s	$\omega/10^3$ rpm	$(c_s)_c/(c_s)_a$
0.70	0.74	6.20	2.50	1.00
2.00	2.12	6.20	2.50	1.00
3.30	3.71	6.20	2.50	1.06
4.60	4.95	6.20	2.50	1.01
5.90	6.48	6.20	2.50	1.04
7.20	7.75	6.20	2.50	1.02
8.50	9.36	6.20	2.50	1.04
9.45	2.36	1.40	2.50	1.04
9.45	2.92	1.40	3.60	1.08
9.45	3.46	1.40	4.90	1.09
9.45	5.19	3.80	1.60	1.06
9.45	6.43	3.80	2.50	1.05
9.45	7.78	3.80	3.60	1.05
9.45	4.22	6.20	0.40	1.05
9.45	8.63	6.20	1.60	1.07
9.45	13.14	6.20	3.60	1.09

$E_d = -0.40$ V, $v = 50$ mV s⁻¹ concentration of NaOH = 0.2 mol dm⁻³

Table III. $(I_p/c_S t_d)$ values for different c_S and t_d values in differential pulse mode.

$c_S/10^{-8}$ mol dm ⁻³	$I_p/10^{-4}$ A	$t_d/10^3$ s	$(I_p/c_S t_d)/As^{-1}$ mol ⁻¹ dm ³
0.90	0.060	1.22	0.546
2.10	0.14	1.22	0.546
3.30	0.215	1.22	0.534
4.50	0.300	1.22	0.546
5.70	0.385	1.22	0.554
16.0	0.550	0.620	0.554
36.0	1.23	0.620	0.551
56.0	1.89	0.620	0.544
76.0	2.50	0.620	0.531
96.0	3.00	0.620	0.504
196	1.45	0.140	0.528
396	2.65	0.140	0.478
596	3.65	0.140	0.437
796	4.47	0.140	0.401
996	5.32	0.140	0.382

Except ^{for} Na₂S concentrations, all other experimental conditions are same as that in the caption of Fig. 5.

Table IV. Comparison of calculated analytical limit for linear potential scan and differential pulse stripping.

Stripping step ω / rpm	$c_l / 10^{-8} \text{ mol dm}^{-3}$	
	Linear potential scan	Differential pulse
0	1.9	2.8
2500	1.9	0.73

Limits were calculated from stripping voltammograms obtained under the following deposition conditions.

($E_d = -0.4 \text{ V}$, $t_d = 620 \text{ s}$, $c_s = 6.0 \times 10^{-7} \text{ mol dm}^{-3}$, $\omega = 2500 \text{ rpm}$)

The limiting concentration (c_l) is the concentration of sulfide at which the peak current is equal to the residual current at the peak potential.

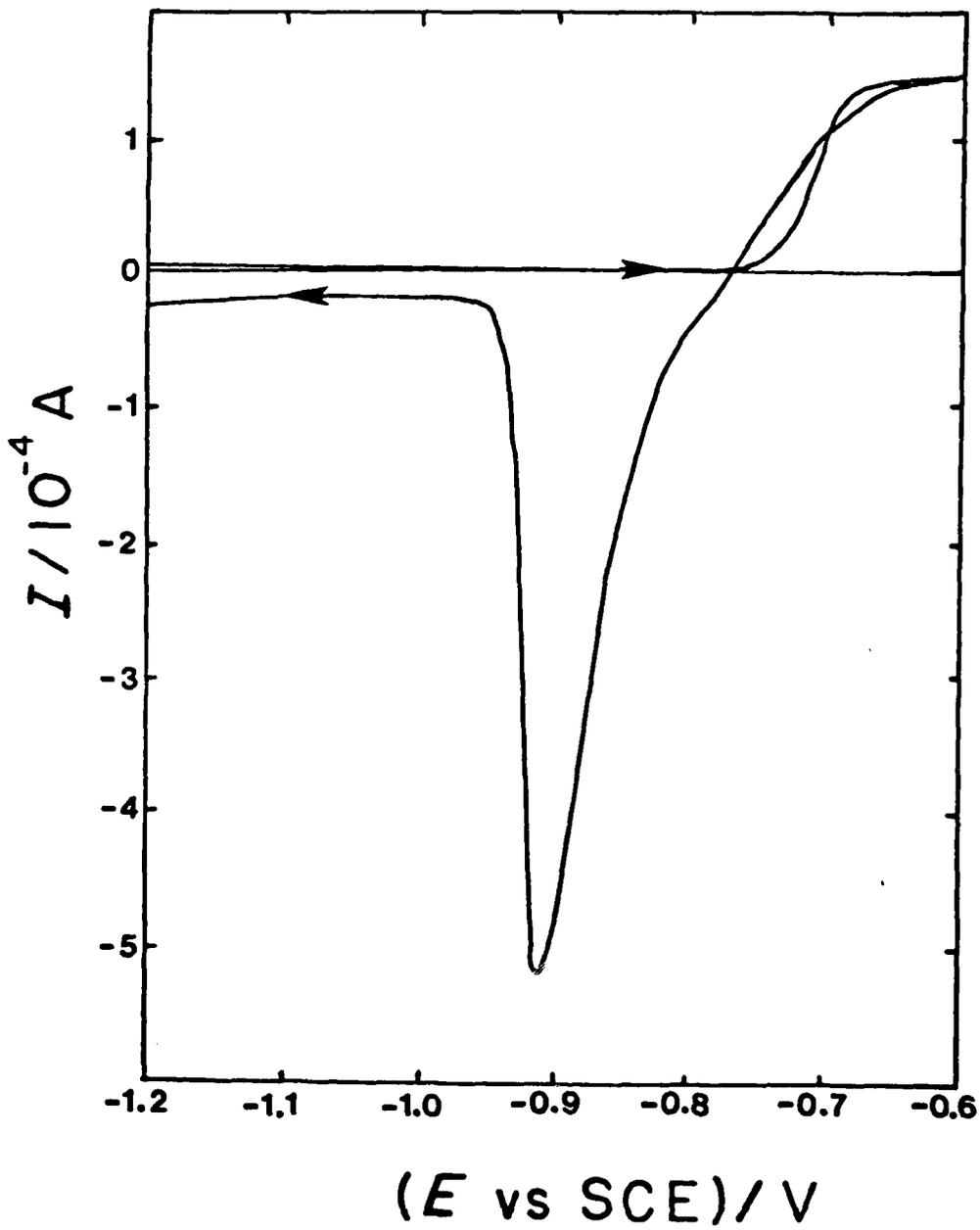


Figure 1

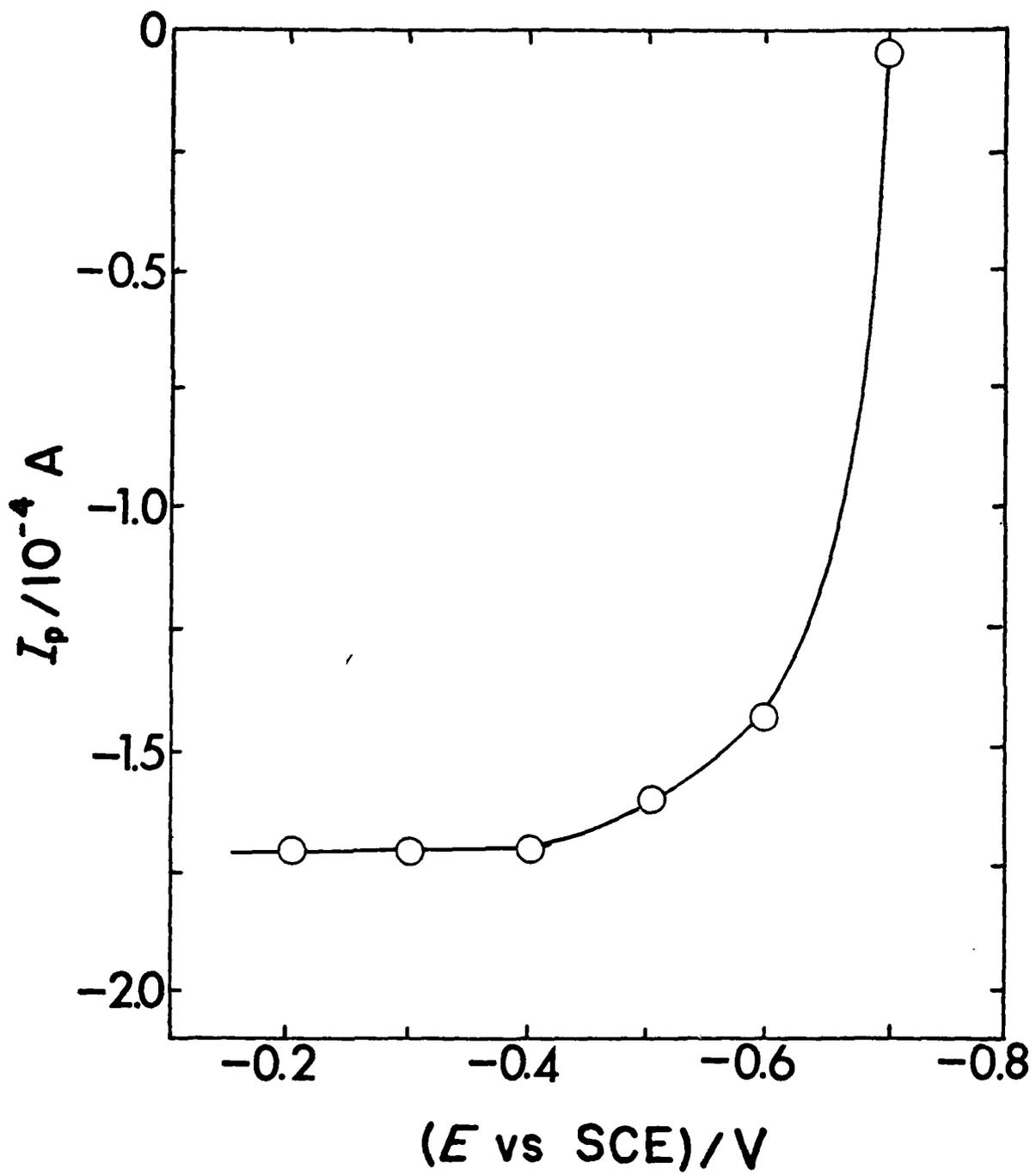


Figure 2

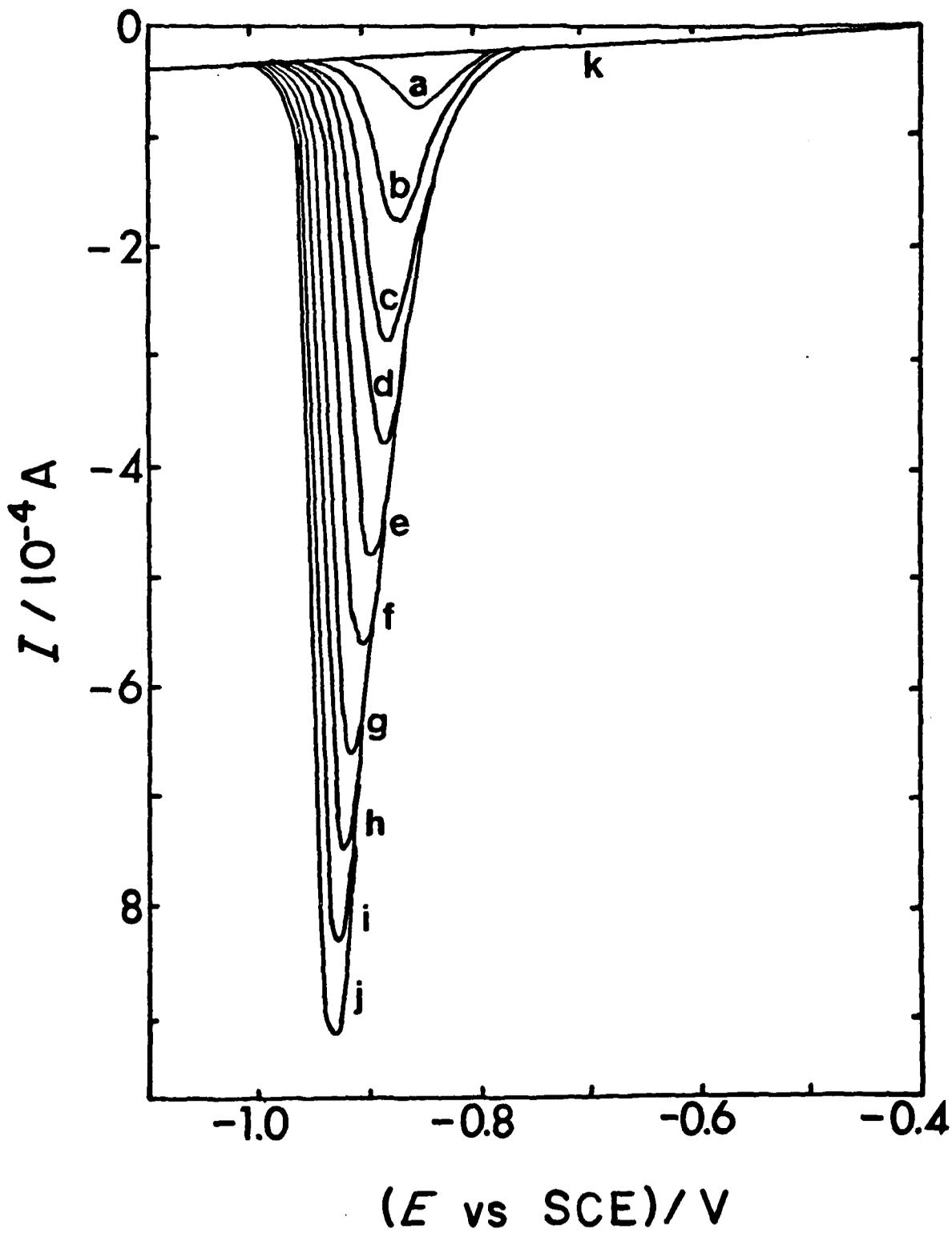


Figure 3

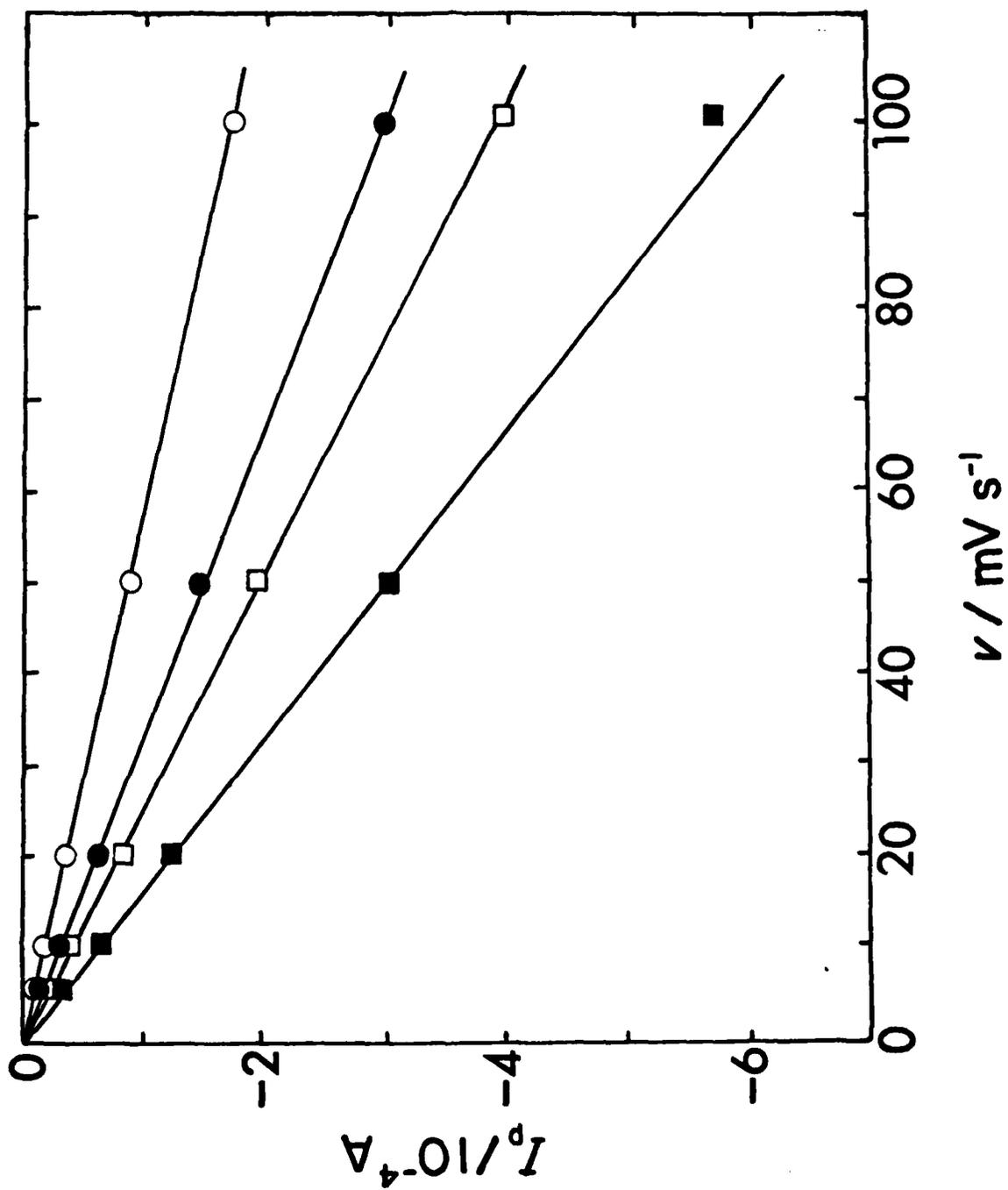


Figure 4

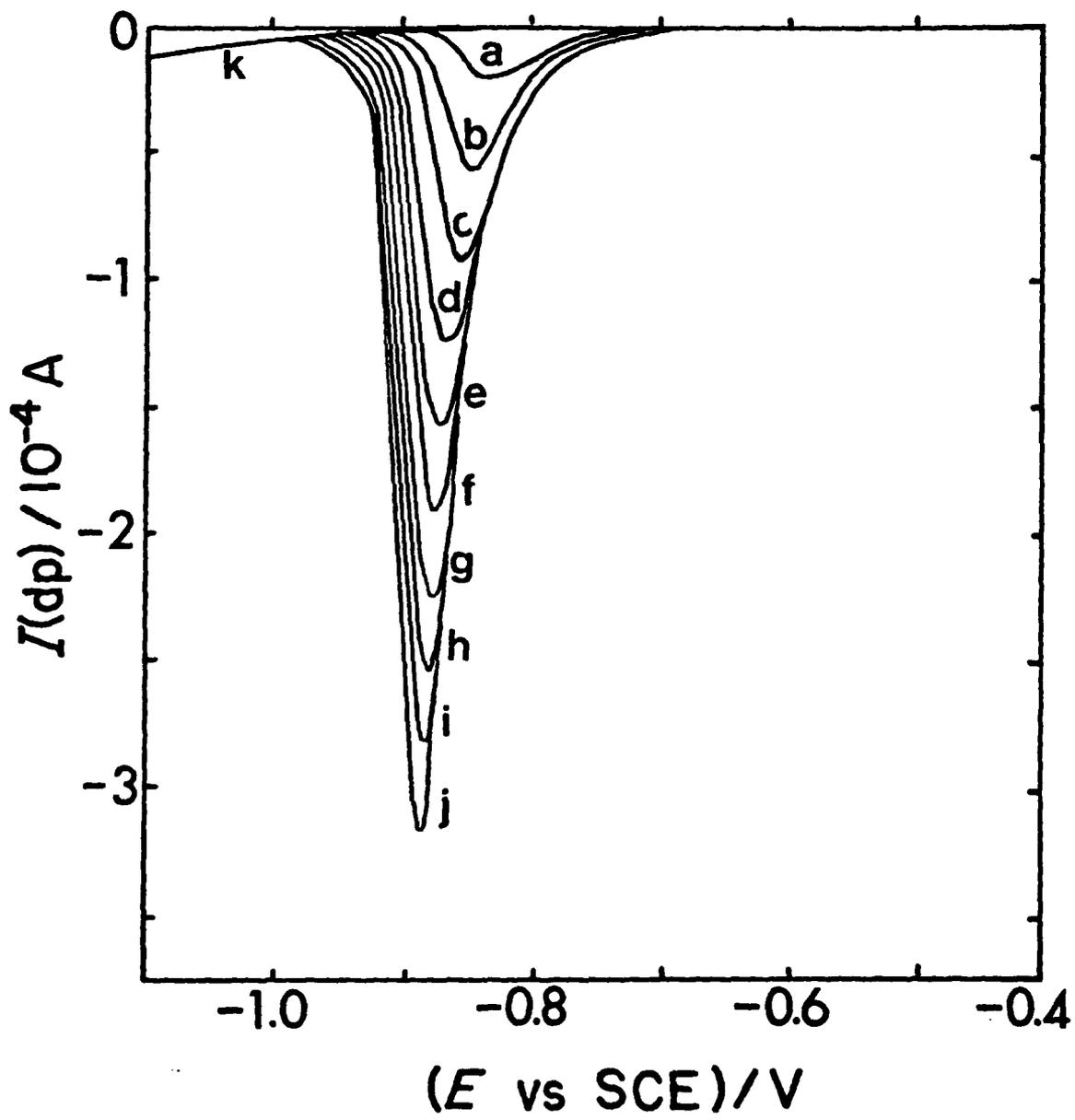


Figure 5

Brief

A rotating silver disc electrode has been employed for the determination of sulfide ion in solution by cathodic stripping voltammetry. Parameters affecting the procedure have been investigated.

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