THE ANODIC STRIPPING VOLTAMMETRY OF TRACE SILVER SOLUTIONS EMPLOYING GRAPHITE ELECTRODES APPLICATION TO SILVER ANALYSIS OF RAIN AND SNOW SAMPLES FROM SILVER IODIDE SEEDED CLOUDS

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INTRODUCTION

Anodic stripping voltammetry (ASV) has proved to be a very versatile technique for the determination of trace elements in the concentration range of $10^{-6}-10^{-10}$ M. The applicability, sensitivity, and limitations of this technique are summarized in detail in two recent and comprehensive reviews by Shain[1] and Barendrecht[2].

Most of the reported analytical applications of ASV have been carried out with the hanging mercury drop electrode provided the elements of interest form amalgams, when deposited, or form anions that react with mercury to form an insoluble film (halides, sulfide)[1,2].For nobler metals than mercury, a solid electrode must be employed, however. Perone has reported the use of a spectrographic grade graphite electrode (SGE) for the determination of silver[3] and showed that when the concentrations of Ag^+ were less than 10^{-7} M, the subsequent stripping voltammograms showed multiple peaks. As the area under the peak(s) is the parameter measured for analytical evaluation, these multiple peaks impose a difficulty. There is more uncertainty of the position of the base line (background current), as the multiple peaks occur over a large voltage range, which results in lower accuracy and precision in measuring the area. Thus, a sharp and narrow mono peak is favored for higher sensitivity, better precision, and accuracy.

The preparation and pretreatment of a solid electrode are also very critical as they determine the reproducibility and accuracy of the results. This pretreatment may include different kinds of processes: (i) Mechanical, such as grinding and polishing; (ii) Chemical, treatment in acids or bases; and (iii) Electrochemical, subjecting the electrode to deposition and stripping potentials alternately. All these factors have been found to have an effect on the reproducibility of the signal as well as the level of the background current[3-5].

In this work the use of pyrolytic graphite (and other graphite forms) were explored, and the pretreatment, the application procedures and conditions of application, were investigated and defined to enable its use for accurate determinations of trace amounts of silver. The physical nature of the deposited silver on the electrode was also investigated by electron microprobe spectroscopy and the deposit was found to be concentrated on specific sites on the electrode surface.

The pyrolytic graphite electrode (PGE), pretreated in a manner found to

yield the most nearly ideal and reproducible anodic stripping voltammograms, has been used for the determination of trace silver in rain and snow samples. A method is described with which it is possible to analyze samples containing silver concentrations as low as 5×10^{-11} M.

EXPERIMENTAL

Apparatus

    The instrumentation employed was constructed from operational amplifier modules and has been described in detail previously[4]. The scan rates employed in the anodic dissolutions were 10–20 mV s^{-1} as indicated below. The anodic stripping voltammograms were recorded by means of a Moseley autograph model 2D-2M X-Y Recorder. The measuring resistor in the current follower[4] was a 100 kΩ $\pm$ 0.1% wire wound element. For high sensitivity measurements, capacitors of 1–5 μF were connected in parallel with this resistor to reduce the noise level in the current output. The reference electrode system, a saturated calomel electrode (SCE), salt bridge, and auxiliary electrode assemblies are illustrated in Fig. 1. The cell of 30 ml solution capa-
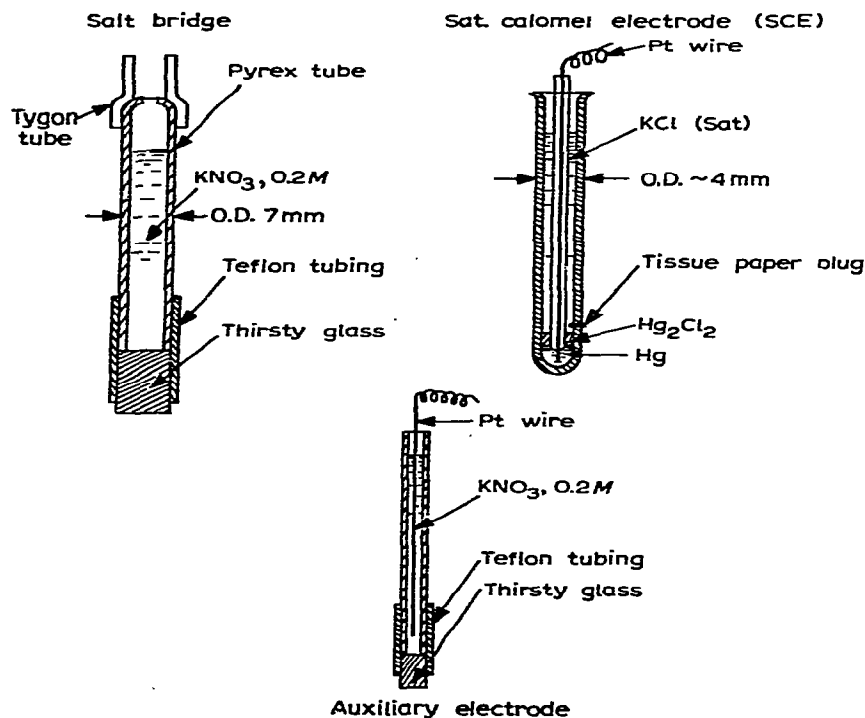

Fig. 1. Schematic diagram of the salt bridge, reference electrode, and auxiliary electrode.

city was constructed from a quartz tube (outside diameter 30 mm). The reference electrode was inserted into the top of the salt bridge. The cell cap was made of Teflon and fitted the cell snugly. Holes were drilled in the cap for insertion of the salt bridge, auxiliary electrode system, and deaeration system. No appreciable surface adsorption of the silver to the cell walls could be detected during the course of any of the anodic stripping analysis experiments (up to a period of 2 h).

nitrite (soluble) and oxide (insoluble). This is in agreement with the finding that NO_3^- must be involved, as such, in the electron-transfer process; in fact, all the attempts[2,5,21] to invoke, in this reduction, the products of the possible dissociations [5,26,27] of NO_3^- (NO_2^+ or O_2):

$$NO_3^- = NO_2^+ + O^{2-} \qquad (23)$$

$$NO_3^- = NO_2^- + \tfrac{1}{2} O_2 \qquad (24)$$

have always failed. As seen, the oxide produced can precipitate on the electrode or dissolve in the melt because of the combined action of diffusion and reaction (c). During the recording of peak I the precipitation prevails, Na_2O is accumulated on the electrode and the reduction of NO_3^- is progressively inhibited. The after-peak limiting current[1,2,5] corresponds to a certain thickness of precipitate at which the rate of dissolution equals the rate of deposition. We have found that this thickness, calculated from the area of peak I (recorded at high potential scan rate to minimize the effect of spontaneous dissolution), is constituted by approximately 300 molecular layers at 229°C. A steady-state similar to the after-peak situation can be readily reached also by polarizing, at a constant potential, an electrode in the region of peak I. It is the case of the massive electrolysis previously described.

Our finding that a chemical process—reaction (c)—is involved in the dissolution, offers a reasonable explanation for the value of 11 kcal* found[1,2] for the temperature coefficient of the limiting current. As pointed out by Swofford and Laitinen, this value is too high to be ascribed to a process uniquely governed by diffusion.

All the possible precipitates in Fig. 6 have been formulated as compounds with sodium and not with potassium, which is also present in the melt. This has been suggested by the fact that the reduction of NO_3^- results in the formation of a current peak only if sodium (or lithium) ions are present; if potassium alone is in the solvent, the current rises without formation of a peak[2,10]. The effect has been recently[10] tentatively explained by postulating a very large difference in solubility between K_2O and Na_2O (or Li_2O).

On the basis of the present study, the alternative interpretation that suggests itself is the difference in reactivity of oxide in the presence of the various alkali metal ions. The absence of the cathodic maximum in the presence of potassium alone can then be due to a fast production of superoxide which is a much more soluble species[23,24] than oxide. It is well known, on the other hand, that oxide (and hydroxide) react much more easily with strong oxidizing agents, such as molecular oxygen, in systems (both solid[28,29] or molten[30]) containing potassium rather than sodium or lithium. A quantitative study of the phenomenon appears, therefore, difficult of fulfilment because at the temperature necessary to work with pure KNO_3 the electrode reactions begin to be strongly complicated by a collateral process implying the corrosive attack[10] of any electrode surface.

Reproducibility and consistency of results

The reproducibility and the consistency of the results reported in this communication were critically contingent on the use of a perfectly dry melt; otherwise

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* 1 kcal = 4.184 kJ.

addition method) and repeating the determination. Standard solutions were prepared in the same manner as previously described[4].

Reagents

Silver-free NH_4SCN was provided by Dr. J. W. Warberton, University of Nevada, Reno, Nevada. All other reagents were reagent grade and were experimentally shown to present no blank problems. The water employed in making all solutions was passed through a mixed bed ion exchanger and then double-distilled (potassium permanganate was added in the first distillation stage).

RESULTS AND DISCUSSION

The characteristic shapes of the stripping voltammograms of submicro solutions of silver ion depend on the type of graphite electrode used and the composition of the supporting electrolyte. The number of dissolution peaks and their individual shapes are also affected strongly by these conditions, as can be seen in Table 1 and

TABLE 1

EFFECT OF MEDIUM AND ELECTRODE MATERIAL ON THE ANODIC DISSOLUTION VOLTAMMOGRAMS OF SILVER SOLUTIONS

Electrolyte medium	Electrode material	Potential of anodic dissolution peaks/ V vs. SCE
0.15 M NH_4OH and	SGE	−0.02, +0.38
0.15 M NH_4NO_3	PGE	−0.05, +0.30*
NH_4OAc–HOAc (total concn. acetate) =0.30 M	SGE	+0.07, +0.18, +0.65
pH=5.0	PGE	−0.01*, +0.20, +0.55*
0.15 M NH_4OH and	SGE	−0.17, +0.05, +0.50
0.15 M NH_4OAc (pH~7)	PGE	+0.10, +0.45*
0.17 M KNO_3	SGE	+0.05, +0.20, +0.40
	PGE	−0.05, +0.17*, +0.40*

* The size of these peaks is very small with respect to the main peak.

Figs. 2 and 3. In general, it was found that more pronounced multiple peaks appear when wax impregnated spectroscopic grade graphic rods, SGE, are used, and that the reproducibility of their shape is poor. It must be ι ⁻phasized here that the shape of the stripping voltammograms were found to vary drastically when using the SGE, although special care was taken at all times to treat the electrodes in the same way. The relative height of the multiple peaks changed and, on occasion, the disappearance of one of the secondary peaks occurred. On the other hand, it was found that the shape and characteristics of the dissolution peak(s) obtained with the PGE was invariant and reproducible. In general, one main peak appeared and one (or two) relatively small secondary peak(s) were observed, as shown in Figs. 2 and 3. The main peak was also considerably sharper than that obtained with a SGE.
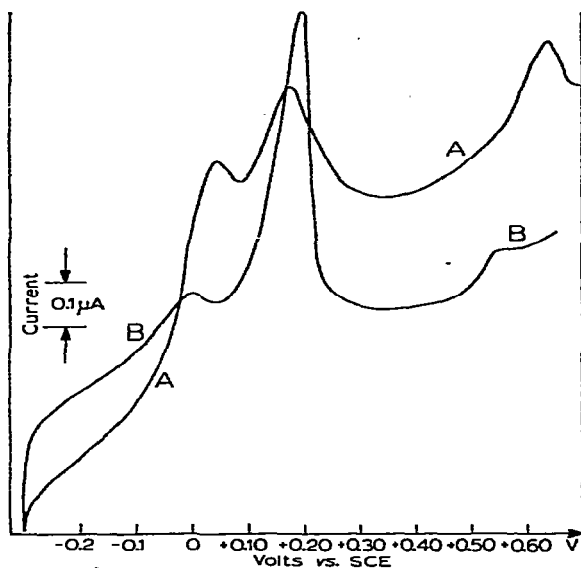
Fig. 2. Anodic stripping voltammograms for a 5×10^{-8} M Ag$^+$ solution in a 0.15 M NH$_4$OAc-HOAc (pH = 5) soln. Sweep rate, 14 mV s^{-1}. The electrodepositions were carried out at -0.60 V vs. SCE for 12 min. (A) SGE, (B) PGE.
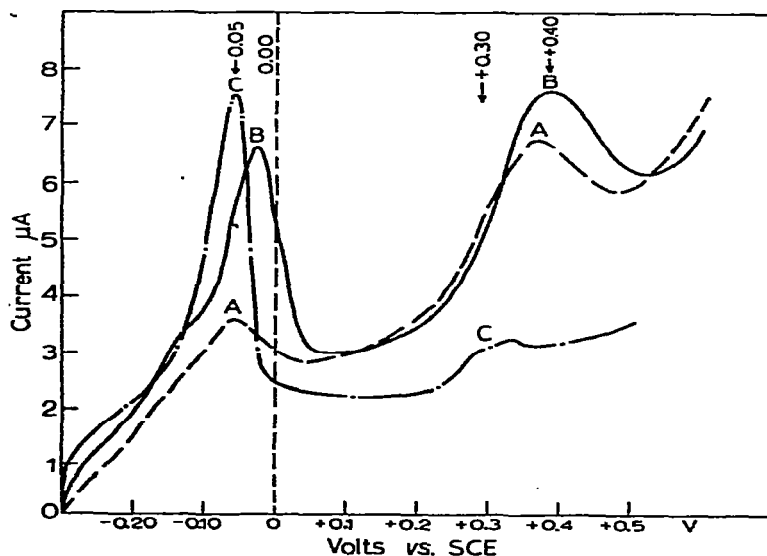

Fig. 3. Anodic stripping voltammogram for a 5×10^{-8} M Ag$^+$ soln. in 0.15 M NH$_4$OH-0.15 M NH$_4$NO$_3$ soln. Sweep rate, 14 mV s^{-1}. The electrodepositions were carried out at -0.60 V vs. SCE. (A) SGE, electrolysis time = 5 min; (B) SGE, electrolysis time = 12 min; (C) PGE, electrolysis time = 5 min.

It is obvious that for analytical work, the PGE is preferable. It must be stressed here that, contrary to the findings of other workers[5], the pyrolytic graphite rods must also be impregnated with wax. This disagreement stems from the differences in current ranges employed. In previously reported studies of the electrochemical behavior of pyrolytic graphite, current levels of the order of 30 μA cm^{-2} (in conventional voltammetry) were used. In comparison, current peaks of the order of 0.03–0.3 μA cm^{-2} were obtained in this work. Accuracy and precision could not be attained with these

low current ranges unless the electrode was wax impregnated. The supporting electrolyte most suitable for silver determination was found to be an ammoniacal buffer of 0.30 M NH_4NO_3–0.60 M NH_4OH solution. The workable voltage span in this solution is from −0.9 to +0.6 V $vs.$ SCE. The dissolution voltammograms for silver on PGE in this solution consist essentially of one peak as shown in Fig. 3. Successive electrolysis on the same electrode surface may result in broadening of the peak, but polishing on the filter paper with ethanol restores the peak to its previous sharpness and height.

The phenomenon of multiple anodic dissolution peaks has been observed by various investigators[6–10]. It has been suggested that the peaks appearing at more positive potential than the formal peak potential of an M,M^{+n} couple represents the first layer of metal deposit bound to the electrode which has a different (greater) bonding energy than the normal bonding in the metal lattice[9]. Propst[10], who used a gold electrode, found that a silver deposition corresponding to a full monolayer coverage of the electrode occurs while electrolyzing at a potential of 0.25–0.75 V more positive ("underpotential") than the potential predicted by the Nernst equation for the macro deposition of silver. In the experiments discussed here, the "monolayer" peak could not be produced alone by employing a more positive potential than was
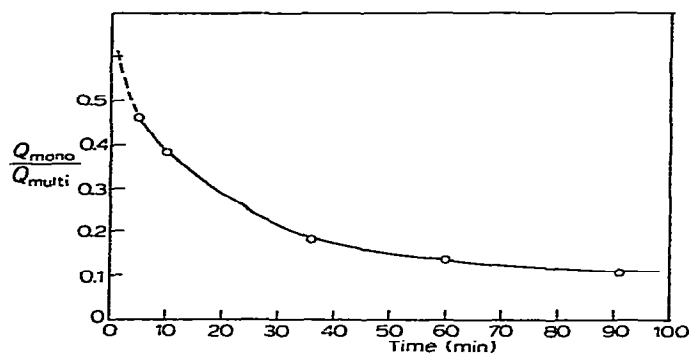

Fig. 4. Variation of the ratio of the area of the "monolayer" peak to the area of the multilayer peak (for the SGE with the ammonia buffer, see Fig. 3).
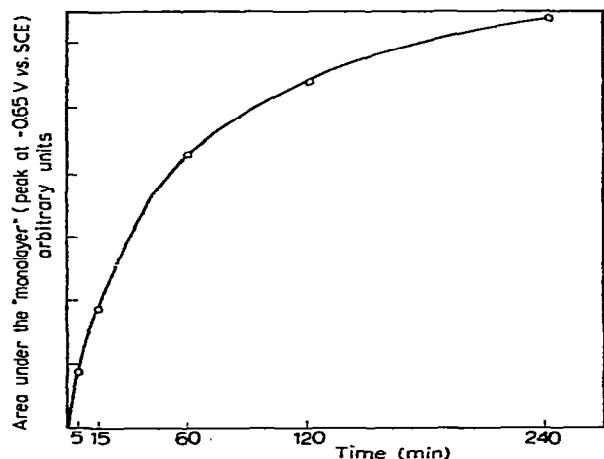

Fig. 5. Variation of the area under the "monolayer" peak at −0.65 V $vs.$ SCE (see Fig. 3) employing a SGE and ammonia buffer, with time.

needed for the normal silver peak. The multiple peaks appeared only whenever the deposition potential was sufficiently negative to produce the "normal" silver anodic dissolution peak.

It was found that (using SGE and ammonia buffer) the "normal" silver peak grows much faster than the "monolayer" peak as a function of electrolyzing time, as shown in Fig. 4. Thus, on the beginning of the electrolysis, the active sites are covered with silver very rapidly. As the electrolysis continues, the multilayer deposit is formed on these sites and, at the same time, coverage of the rest of the surface proceeds, but at a slower pace (Fig. 4). When the electrolysis is carried out for a long enough period, the "monolayer" peak reaches a maximum value as shown in Fig. 5. From results shown in this Figure, it was calculated that the area available for deposition is only about 50% of the total apparent geometric area and, therefore, did not correspond to monolayer coverage. It is interesting to note that this is in good agreement with findings by Matson[11] who studied the mercury film on SGE.

It is of interest to speculate as to why the two types of graphite demonstrate such a large difference in properties. The probable answer can be found in their different structure. The pyrolitic graphite is an almost perfect single crystalline form[4,5]. The graphite plane (two dimensional crystal lattice of fused rings, ab plane) is used as the electrode surface[4]. In the grinding process, the single plane is broken, and the exposed (virtually smooth) surface is really made up of various broken planes. One can assume that there are certain sites on this surface more favored energetically for deposition, but the SGE, on the other hand, is polymicrocrystalline in nature and will have many more active sites. Therefore, the deposition of silver occurs on many sites at once and more deposit of the "monolayer" type deposit is obtained.
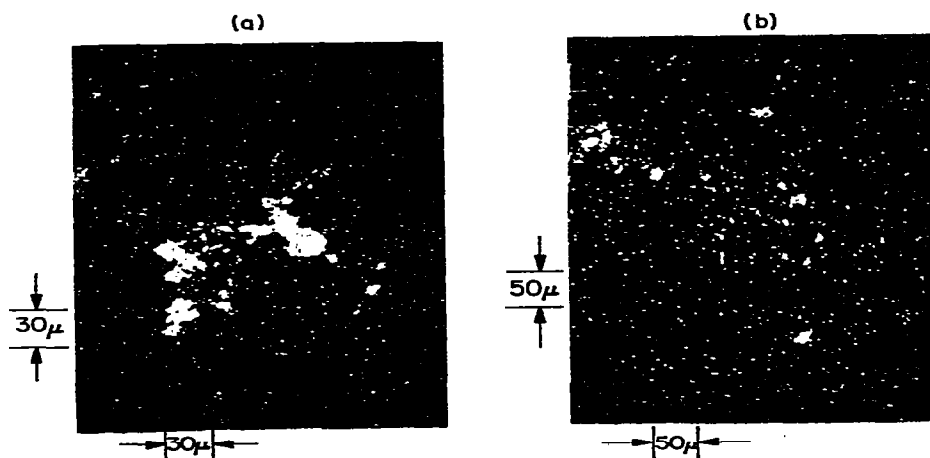

Fig. 6. X-ray fluorescence of a silver deposit on PGE. The deposit was obtained on electrolysis of a 2×10^{-6} M Ag^+, 0.1 M NH_4OAc–0.1 M $HOAc$ soln. at -0.75 V $vs.$ SCE. Electrolysis time, 90 min.

Electron microprobe studies were undertaken to explore further the character of the silver deposit on the electrode. As the sensitivity of the technique is not enough to work with the "monolayer" deposits obtained from solutions of the 10^{-8} M range, an attempt was made to observe the pattern nature of the deposit from higher con-

centration of Ag^+, and to try and correlate these patterns with electrode behavior of the SGE and PGE.

The samples employed were 2×10^{-6} M in Ag^+ and were electrolyzed for 90 min at -0.75 V vs. SCE. When the electrolysis was stopped, the electrode was rinsed with acetone, and a disc for study was cut[4]. When the disc of the pyrolytic graphite (with the silver deposit on it) was viewed through a microscope, a few spots of silver could be found, but in general, the electrode surface appeared homogeneous. These specks of deposit appeared very clearly (Fig. 6, a, b) on the X-ray fluorescence micrographs. Such high concentration silver deposits could not be found on the SGE discs. These discs appeared to be homogeneous all over the surface and the X-ray fluorescence density of these samples was higher than that found for the "homogeneous"
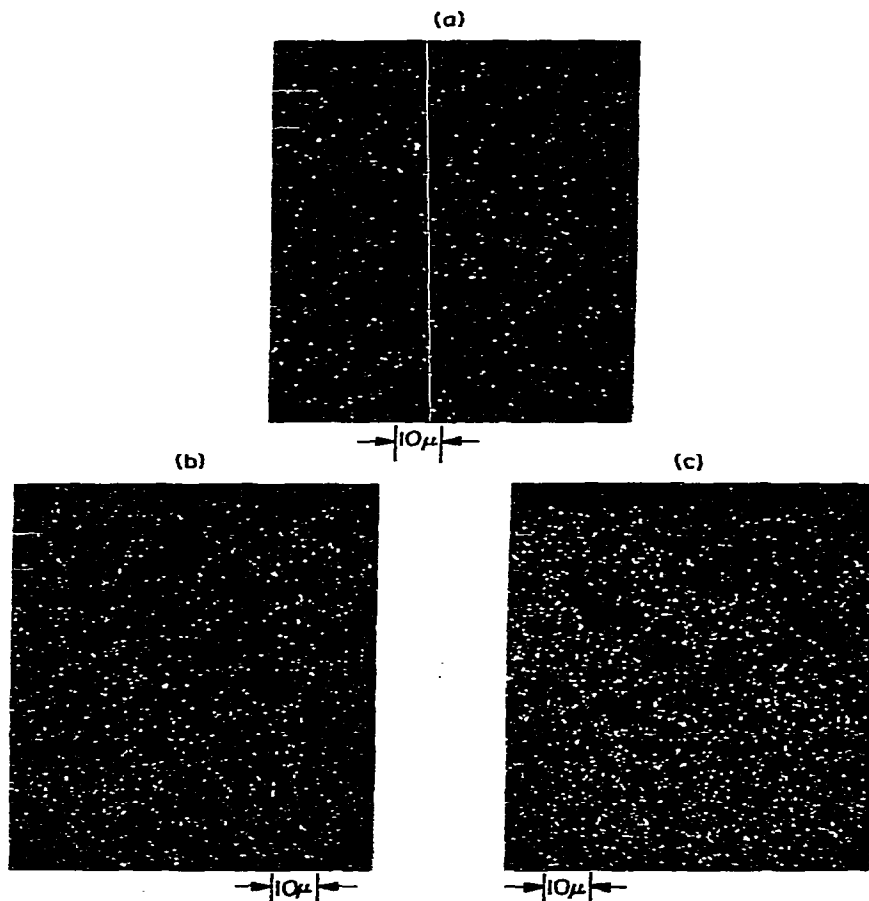

Fig. 7. X-ray fluorescence of silver deposits. Electrolysis at -0.70 V vs. SCE for 90 min from a 5×10^{-6} M Ag^+, 0.1 M NH_4OAc. (a) Blank obtained for PGE disc; (b) "homogeneous" areas of deposit, PGE disc; (c) deposit on SGE.

areas (between spots) for the pyrolytic graphite discs (Fig. 7, a, b, c). Although these experiments show a tendency for a different formation of silver deposits or a difference in the number of active sites on the two graphites, they cannot be directly correlated with the experimental observation and mechanism of multiple dissolution peaks because of the higher deposition concentration used.

APPLICATION OF ANODIC STRIPPING VOLTAMMETRY TO THE DETERMINATION OF SILVER TRACES IN SNOW SAMPLES

Weather modification by cloud seeding has become a common practice in many regions. The most usual agent used in seeding is crystalline silver iodide. The seeding is performed by either ground-based or airborne generators. Analysis of the snow or rainfall in these regions enables investigation of the effectiveness of the seeding process and indicates the most effective locations for placing the generators in order to modify the precipitations. The expected concentration range of silver in the precipitation is about $10^{-8}-10^{-11}$ M[12]. The most effective micro method of silver analysis is that developed by Warberton, employing neutron activation (NAA)[12] which utilizes the nuclear reaction ^{109}Ag $(n\gamma)$ ^{110}Ag. As the half life of the resulting ^{110}Ag is 24 s a very sensitive γ spectrum for silver is obtained. A pre-concentration prior to the activation step employs a cation exchange resin which is eluted with 0.1 M NH_4SCN. The detection limit of this method is about 5×10^{-11} M but the accuracy of determinations of lower than 10^{-10} M concentrations is very poor[12]. As will be shown later, ASV is much more sensitive and because of simple instrumentation has the potential of allowing the analysis to be carried out under field conditions.

It was found that concentrations of silver higher than 3×10^{-9} M could be determined by direct ASV. In the case of lower concentrations, a preconcentration step was also employed.

Reproducibility and accuracy of direct ASV were checked on standard silver solutions of 4×10^{-9} M and reproducibility of the peak areas was better than $\pm 5\%$. On standard addition to bring the solutions to 6×10^{-9} M, the agreement between expected and experimental results was better than $\pm 7\%$. Electrolysis duration needed for this concentration level was 15 min.

In order to determine lower Ag^+ concentrations, a preconcentration step, for silver traces, which was also essential to Warberton's method[12], was used in this work. An enrichment factor of about 80 was obtained by using 1 l samples which were passed through a Dowex 50W–X8 cation exchange column of 25.0×10.0 mm, and eluting with 24 ml of 0.04 M NH_4SCN. One ml of a mixture of one part concentrated HNO_3, one part H_2O, and one part NH_4OH was used to bring the total volume to 25 ml. Thus samples as low as 4×10^{-11} M can be determined.

It was found that a high concentration of NH_4SCN (greater than 0.05 M) caused a splitting and broadening of the stripping peaks. On the other hand, in order to obtain good elution efficiency ($>80\%$), the NH_4SCN concentration must be larger than 0.02 M. A 0.04 M NH_4SCN could be used without impairing the efficiency of the elution process and without causing a noticeable change in the stripping voltammograms. Also, single and sharp stripping peaks were developed when the supporting electrolyte was 0.3 M NH_4NO_3–0.6 M NH_4OH.

Typical analytical results

The results of a few sample analyses of precipitation for Ag^+ are reported below to demonstrate the applicability of the above procedures. Snow samples were supplied by M. J. Warberton of the Desert Research Institute, University of Nevada, Reno, Nevada. From previous neutron activation analysis (NAA) of these samples, it was shown that the samples could be divided into 2 groups: Group (A) $[Ag^+] > 10^{-9}$

M and Group (B) $[Ag^+] < 10^{-9}$ M. A set of replicate snow samples from group A, which were designated sample No. 23, were analyzed directly by transferring 25 ml of each sample into the cell and adding to it 1 ml HNO_3 (concentrated HNO_3, diluted 1 : 1) and 1 ml of concentrated NH_4OH (the resulting solution was 0.3 M NH_4NO_3, 0.3 M NH_4OH). The results are shown in Table 2.

TABLE 2
DIRECT ANODIC STRIPPING ANALYSIS OF SNOW SAMPLES

Sample No. 23	Concn. measured $\times 10^9$ M	Mean concn.	Neutron activation value[12]
6.8 7.2 7.6 6.3		7.0×10^{-9} ±6%	20×10^{-9} ±6%

To check further the above values, the concentration was determined after employing the ion exchange enrichment step. In this case 25 ml of sample No. 23 was passed through the ion exchange column and the silver was eluted with 25 ml of 0.04 M NH_4SCN into the cell that held 1 ml of 1 : 1 diluted concentrated HNO_3 and 2 ml of concentrated NH_4OH. The concentration of silver found was 6.2×10^{-9} M which is in satisfactory agreement with the results found by the direct method.

A set of replicate snow samples from group B, which were designated samples No. 12 and 25, were preconcentrated using the same ion exchange procedures used to concentrate silver from the two sets of samples of group B. As stated above the sample volume was 1000 ml. The results of the analyses are shown in Table 3.

TABLE 3
RESULTS OF ANALYSIS OF GROUP B SAMPLES EMPLOYING A PRECONCENTRATION STEP

Sample No.	Concn. found $\times 10^{11}$ M	NAA[12] results $\times 10^{11}$ M
25	10	7.8
12	4.8	1.1

From these results it can be seen that the ASV merits serious consideration for trace Ag^+ analysis of precipitation samples as a standard method. These preliminary results have not established which method results in the least absolute error in determination of 10^{-11} M or lower concentrations. Further studies are necessary to determine this fact but the analytical procedure as well as instrumentation is far simpler with ASV.

SUMMARY

The characteristics of the anodic stripping curves obtained from 10^{-11}–10^{-7} M Ag^+ have been studied using pyrolytic graphite and wax impregnated spectrographic grade carbon electrodes. It was found that the stripping curves on pyrolytic graphite electrodes (PGE) had essentially only one sharp dissolution peak, while those for wax impregnated carbon (SGE) exhibited multiple dissolution peaks. The nature of the Ag deposits was studied by X-ray fluorescence employing an electron microprobe which showed that PGE had a few preferred sites for deposition but the SGE exhibited a uniform distribution of the deposit. The optimum solution conditions, electrode pretreatments, and procedure are described, as well as the results of the analyses of snow samples containing 10^{-8}–4×10^{-11} M Ag^+.

REFERENCES

1 I. SHAIN in J. M. KOLTHOFF AND P. J. ELVING (Eds.), *Treatise on Analytical Chemistry*, Part I, Vol. 4, Interscience Publishers, New York, 1962.
2 E. BARENDRECHT in A. J. BARD (Ed.), *Electroanalytical Chemistry*, Vol. 2, M. Dekker, New York, 1967.
3 S. P. PERONE, *Anal. Chem.*, 35 (1963) 2091.
4 B. H. VASSOS, Ph. D. Dissertation, Univ. of Michigan, 1964; H. B. MARK, JR., F. J. BERLANDI, B. H. VASSOS AND T. H. NEAL, *Proc. 1965 Intern. Conf.: Modern Trends in Activation Analysis*, Texas A and M Press, 1966.
5 I. FRIED, Ph. D. Dissertation, Univ. of Michigan, 1964.
6 K. GARDINER AND L. B. ROGERS, *Anal. Chem.*, 25 (1953) 1393.
7 M. M. WECHOLSON, *J. Amer. Chem. Soc.*, 79 (1957) 7.
8 B. H. VASSOS AND H. B. MARK, JR., *J. Electroanal. Chem.*, 13 (1967) 1.
9 L. B. ROGERS AND A. F. STEHNEY, *J. Electrochem. Soc.*, 95 (1949) 25.
10 R. C. PROPST, *J. Electroanal. Chem.*, 16 (1968) 319.
11 W. R. MATSON, Ph. D. Dissertation, Mass. Inst. of Tech., 1967.
12 J. A. WARBERTON AND L. G. YOUNG, Reprint Series No. 97, Desert Research Inst., Univ. of Nevada, Reno, Nevada, 1967.