# THE FEASIBILITY OF USING TANTALUM METAL AS INDICATOR ELECTRODE IN PRECIPITATION TITRATION REACTIONS

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## Abstract

Tantalum metal was found to serve as an excellent indicator for potentiometric precipitation titrations. The experimental results were discussed in terms of the potential arrests and potential shifts upon addition of the titrant.

The obtained results for 0.05M halogen solutions revealed that when tantalum electrode is coupled with SCE or Pt electrodes, sharp potential jumps and distinct end points were obtained in the titration of $Cl^-$, $Br^-$ and $I^-$ solutions against 0.057M $AgNO_3$ solution in both forward and backward titration techniques. On the other hand, Ta/Ag systems in forward titrations of $Br^-$ and $Cl^-$ solutions behave similarly. While in backward titration, the end point is determined by presence of a sharp potential peak in the positive direction. In $I^-$ solutions, Ta/Ag system illustrates a sharp potential peak in both forward and backward titration curves. Results for 0.1M halogen solutions revealed that the equivalence volumes in forward titrations for $Br^-$ and $I^-$ solutions in the four systems are very near to the calculated ones. Concerning $Cl^-$ solutions, the volume magnitudes corresponding to the potential jumps are so far from calculated values in all systems used. For $I^-$ solution, in backward titration, the order of increasing potential jumps of tantalum systems was as follows:

Ta/ Pt < Ta/ Ag < Ta/SCE system.

The shape of the titration curves depends upon the kind of halogen and its concentration as well as on the type of system used and type of titration when the experiment is carried out.

**Key words**: Potentiometric, Platinum, Silver, Tantalum, Passive films, Indicator, Titration

## Introduction

In potentiometric titrations, the titrant is added to a solution and the potential between an indicator and a reference electrode is measured. The reaction must involve the addition or removal of an ion for which an electrode is available. The end point corresponds to the maximum rate of change of potential per unit volume of titrant added. This technique is one of the greatest applications used to evaluate the detection limit in ion selective electrodes [1-4], determine the low concentrations of anionic [5-10] and cationic surfactants [11]. In addition, to determine the solubilities of bivalent metal oxides in a molten eutectic mixture [12]. In aqueous solutions, tantalum electrode has frequently been used in several methods of analysis such as potentiometric and amperometric titrations [13]. The sensitivity of this electrode

depends on the nature and thickness of the oxide film on its surface. This film may be naturally formed in air or by electrolytic oxidation. Ta–$Ta_2O_5$ electrode has been used in potentiometric titration as indicator electrode for the determination of the concentration of oxide ions in molten salts [14, 15] and as a pH indicator electrode in aqueous media [16-18].

In the present study, the use of the bimetallic combination of SCE, Pt, and Ag (as reference electrodes) with tantalum metal (as an indicator electrode) was investigated to study the ability of such combinations to be used for potentiometric determination of equivalence points in precipitation reactions.

**Experiment**

The chemicals required were of different origins but of analytical reagent grade. All solutions were prepared by dilution from a concentrated stock solution stored in a glass bottle using bi-distilled water. The solutions were standardized according to recommended procedures [19]. The titrant dosage rate was 0.5 $cm^3$/min, each system was titrated twice at least.

Tantalum electrode was prepared from a cylindrical rod of spectroscopically pure tantalum metal of 0.096 $cm^2$ area supplied by Johnson Matthey, England. A stout copper wire lead was affixed at one end by mechanical jamming. The electrode surface was mechanically polished using 320, 600, 800 and 1000 grid emery papers. Then, it was rubbed against soft cloth to acquire a silvery bright appearance. The potential of electrode was measured relative to saturated calomel electrode (SCE), platinum sheet with area of 4$cm^2$ and silver wire of 0.12$cm^2$ area. For the sake of comparison, the titrations were followed simultaneously with Pt/ SCE cell.

The forward titrations were carried out by taking the reagent (KI, KBr and KCl) in the vessel and $AgNO_3$ is added from a burette and the EMF is plotted against the volume of titrant. The back titrations were also carried out by adding the halogen solution from the burette. A digital potentiometer with a sensitivity of 0.1mV (KEITHLEY, model 175, USA) was used for potential measurements.

**Results And Discussion**

The potentiometric titration curves represented the variation of the potential of Pt/ SCE, Ta/ SCE, Ta/ Pt and Ta/ Ag systems during the titration process.

In forward titrations, for all systems in different 0.05M halogen solution, sigmoid curves are obtained except in I⊖ solution of Ta/Ag system showing a sharp potential peak in the negative direction (Figure 1). In backward titrations, the curves

behave reversibly except in Br$\ominus$ and Cl$\ominus$ solutions of Ta/Ag systems (Figures 2and 3) showing a sharp potential peak in the positive direction.

In forward titrations, the magnitudes of jumps of Ta-systems are generally higher than those of Pt/SCE systems (Table 1), indicating the ability of the use of Ta electrode as an indicator electrode. The same behavior observed for I$\ominus$ solutions in reverse titration. While in Br$\ominus$ and Cl$\ominus$ solutions, the increases of potential jumps follow the order:   Ta/Pt < Pt/SCE < Ta/SCE

Ta/Ag systems in the three halogen solutions have a characteristic behavior. It was noted that before and after the end point, the potential has small changeable values. In I$\ominus$ solutions, negative and positive peaks in forward and backward titration curves were observed respectively. The height of the peak has no indication but the tip represents the equivalence volume. In Br$\ominus$ and Cl$\ominus$ solutions, the same behavior occurs for backward titrations. While in forward titrations, the negative peak is too little and the potential jumps predominate from which the equivalence volume is calculated.

In forward titrations of Cl$\ominus$ solutions, a continuous increase of potential is observed before the presence of S- shape using Ta- systems.  In presence of chloride ions, the efficiency of oxide formation decreased due to the preferential adsorption of Cl$\ominus$ ions by the oxide. Subsequently, the properties of the oxide film surface are greatly influenced, similarly to the behavior of Nb electrode in Cl$\ominus$ solutions [20]. Thus, the electrode behaved differently and the potential elevated till a sufficient amount of titrant cause a decrease in Cl$\ominus$ ions concentration (Figure 3).  On  the other hand, the behavior of tantalum metal in Br$\ominus$ solution might be explained since Ta is readily passivated in aqueous solutions forming pentoxides according to the reaction [21]:

$$2 \text{ Ta} + 5 \text{ H}_2\text{O} = \text{Ta}_2\text{O}_5 + 10 \text{ H}^+ + 10 \text{ e}\ominus \quad (1)$$
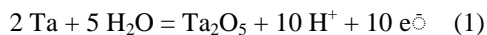
Where, pentoxide film of this metal possesses high protective properties. The behavior of iodide ions was similar to those of Br$\ominus$ ions. It confirms the 1:1 stoichiometry of the chemical reaction which takes place in the solution and fast kinetics of the reaction at the electrode [22].

The experimental equivalence volumes are coincide or located so close to those calculated ones being 1.32, 2.19 and 4.38 ml for forward titration and 1.71, 2.85 and 5.70 ml for backward titration for 1.5, 2.5 and 5.0 ml solution respectively (Table 1).

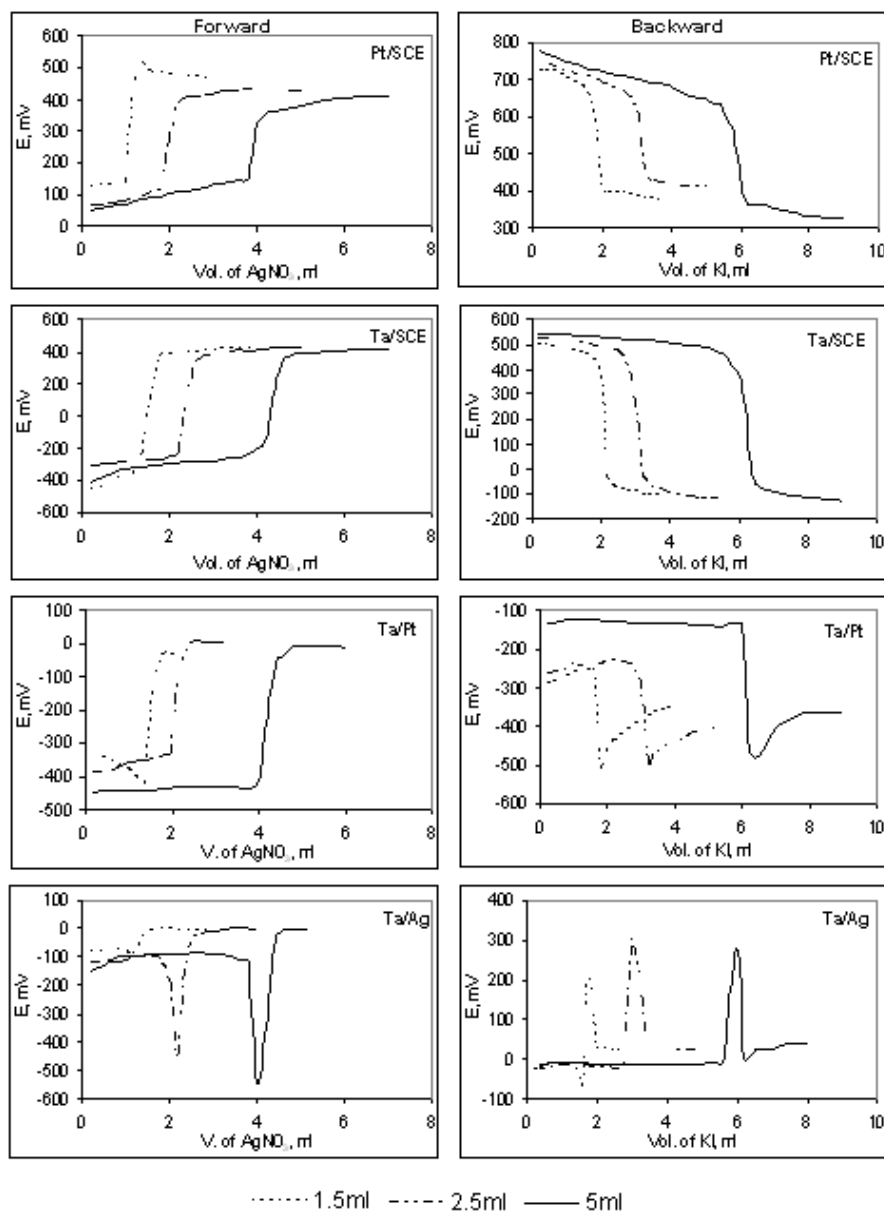**Figure (1): Forward and backward titration curves of 1.5, 2.5 and 5ml. of 0.05N KI solution against 0.057N AgNO₃ solution.**

Figure (2): Forward and backward titration curves of 1.5, 2.5 and 5ml. of 0.05N KBr solution against 0.057N AgNO$_3$ solution.

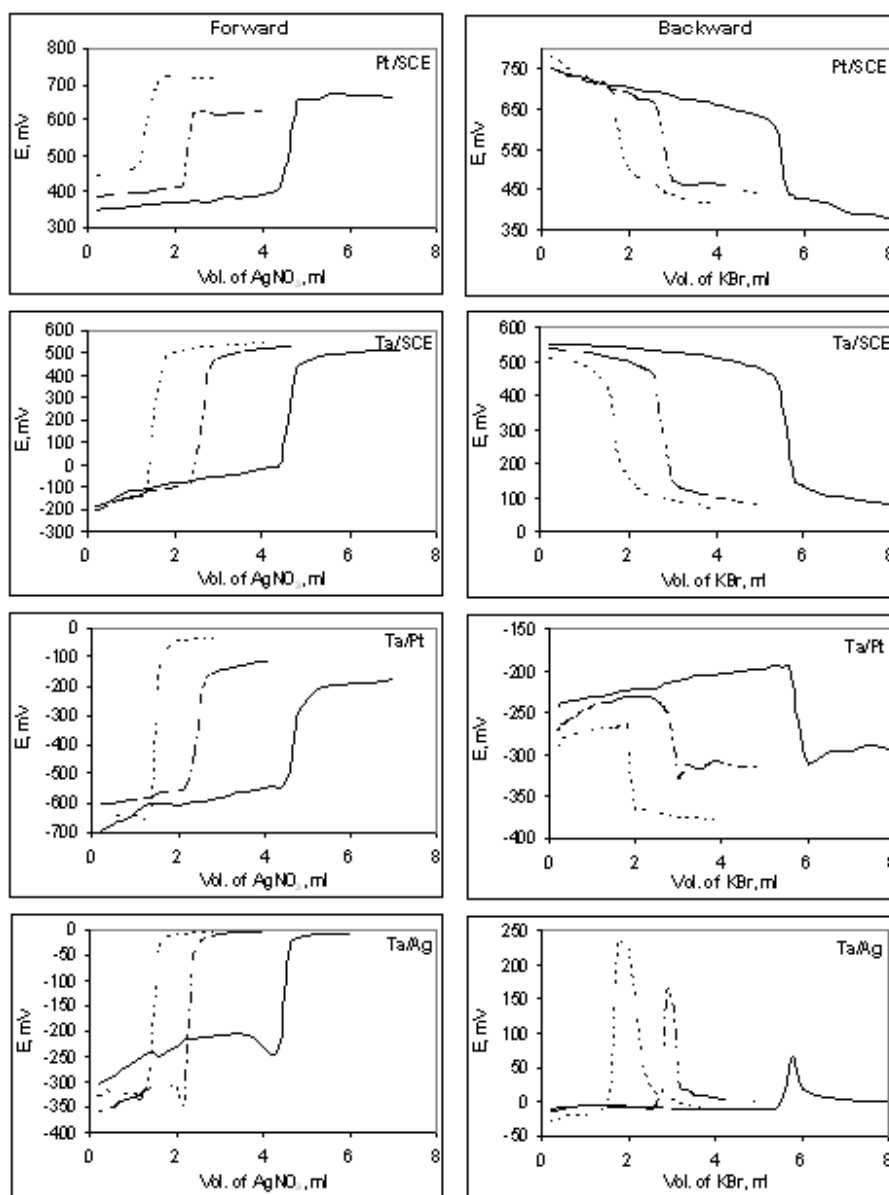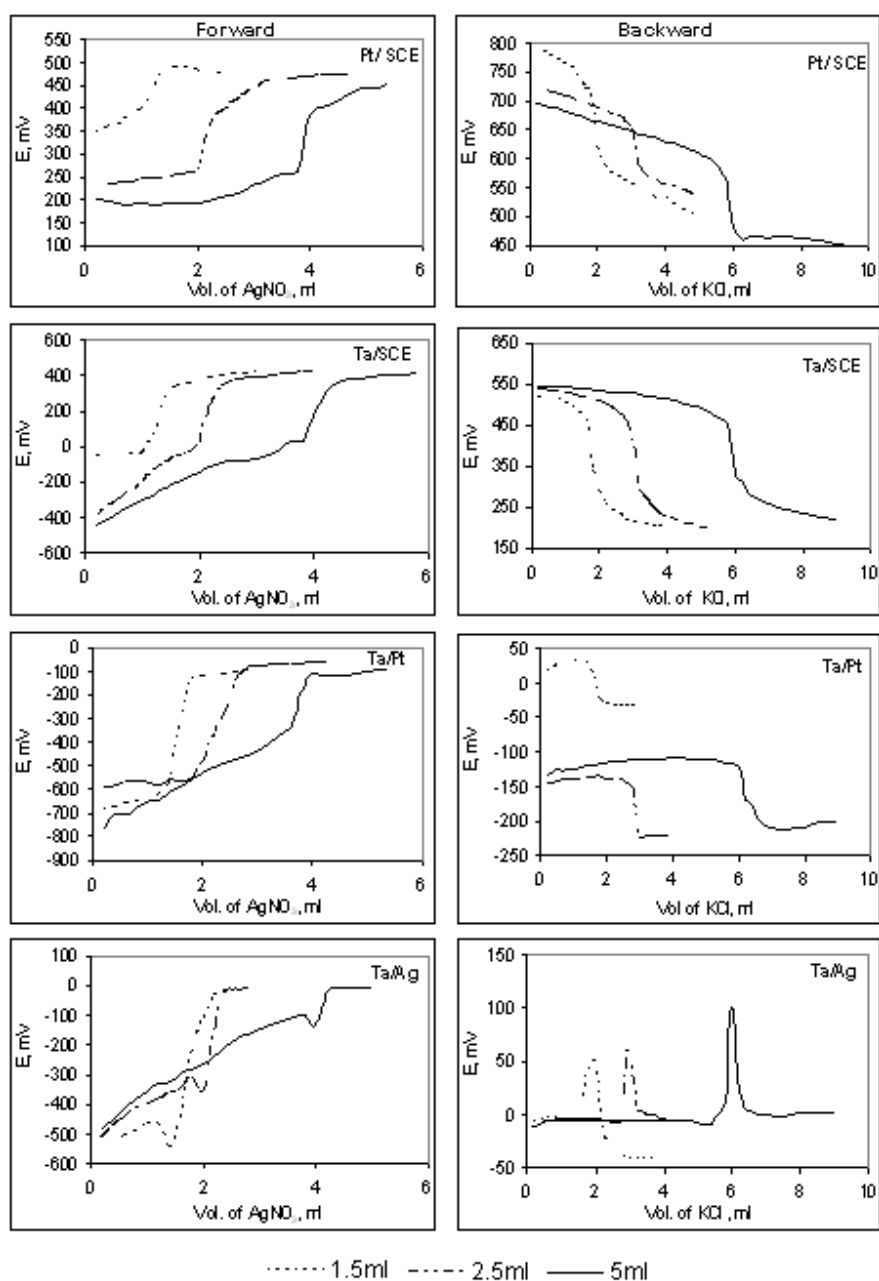**Figure (3): Forward and backward titration curves of 1.5, 2.5 and 5ml. of 0.05N KCl solution against 0.057N AgNO₃ solution.**

**Table (1): Comparison among different electrode systems in precipitation titration reactions for   0.05M halogen solutions**

| System | Vol. (ml) | 0.05NKI | | 0.05N KBr | | 0.05N KCl | |
|---|---|---|---|---|---|---|---|
| | | Equivalence Vol. ( ml) | Jump height (mV) | Equivalence Vol. ( ml) | Jump height (mV) | Equivalence Vol. ( ml) | Jump height (mV) |
| **Forward** | | | | | | | |
| **Pt/SCE** | **1.5** | 1.2 | 384 | 1.4 | 272 | 1.2 | 93 |
| | **2.5** | 2.0 | 323 | 2.2 | 213 | 2.4 | 208 |
| | **5.0** | 4.0 | 248 | 4.7 | 282 | 3.9 | 137 |
| **Ta/SCE** | **1.5** | 1.6 | 768 | 1.6 | 649 | 1.2 | 424 |
| | **2.5** | 2.4 | 673 | 2.6 | 614 | 2.4 | 434 |
| | **5.0** | 4.5 | 665 | 4.6 | 521 | 4.2 | 409 |
| **Ta/Pt** | **1.5** | 1.6 | 405 | 1.5 | 607 | 1.5 | 442 |
| | **2.5** | 2.2 | 333 | 2.4 | 437 | 1.9 | 470 |
| | **5.0** | 4.2 | 430 | 4.6 | 355 | 3.8 | 221 |
| **Ta/Ag** | **1.5** | 1.4 | 84 | 1.5 | 321 | 1.7 | 534 |
| | **2.5** | 2.2 | 336 | 2.4 | 341 | 2.2 | 344 |
| | **5.0** | 4.0 | 433 | 4.6 | 241 | 4.1 | 124 |
| **Backward** | | | | | | | |
| **Pt/SCE** | **1.5** | 1.8 | 263 | 1.8 | 188 | 2.0 | 171 |
| | **2.5** | 3.2 | 257 | 2.8 | 227 | 3.0 | 105 |
| | **5.0** | 5.8 | 282 | 5.4 | 196 | 6.1 | 127 |
| **Ta/SCE** | **1.5** | 2.0 | 584 | 1.8 | 407 | 2.0 | 318 |
| | **2.5** | 3.0 | 639 | 2.8 | 404 | 3.0 | 286 |
| | **5.0** | 6.2 | 619 | 5.5 | 421 | 6.0 | 212 |
| **Ta/Pt** | **1.5** | 1.7 | 274 | 1.9 | 109 | 1.7 | 63 |
| | **2.5** | 2.8 | 290 | 2.8 | 96 | 3.0 | 85 |
| | **5.0** | 6.2 | 351 | 5.8 | 151 | 6.5 | 101 |
| **Ta/Ag** | **1.5** | 1.8 | 266 | 1.5 | 209 | 2.0 | 49 |
| | **2.5** | 3.0 | 323 | 2.7 | 174 | 3.0 | 56 |
| | **5.0** | 6.0 | 383 | 5.6 | 77 | 6.0 | 92 |

The effect of increasing halogen ions concentration to 0.1M was also studied. Sigmoid curves are obtained with all systems used, except for Ta/Ag system in backward titrations. In this system, at the end point, the curves have a sharp potential peak in the positive direction for $I^-$ and $Br^-$ solutions and in the negative direction for $Cl^-$ solution corresponding to the equivalence point. The magnitude of jumps and the experimental equivalence volumes were tabulated in Table 2.

The experimental equivalence volumes in forward titrations of $Br^-$ and $I^-$ solutions in the four systems are very near to the calculated ones being 2.63, 4.38 and 8.77ml for 1.5, 2.5 and 5.0ml halogen solution, respectively (Table 2). Besides,

the potential jumps in Br$\ominus$ solutions are always higher than those of I$\ominus$ solutions except for Ta/Pt system. The increase in the potential jumps might be explained taking into consideration the solubility product of AgI is much smaller than that of AgBr (where, Ksp =5.2x10$^{-13}$ and 8.3x10$^{-17}$ for AgBr and AgI, respectively) [23].

For I$\ominus$ solutions, the heights of jumps are ascending in the following order: Ta/Ag < Ta/Pt < Ta/SCE. While for Br$\ominus$ and Cl$\ominus$ solutions there are no trends for ascending or descending the jumps in the different systems. Furthermore, for Cl$\ominus$ solutions, the volume magnitudes corresponding to the potential jumps are so far from calculated values in all systems used. This may be due to the interference of Cl$\ominus$ ions from high concentration in the salt bridge to low concentrated solution. This interference increases the actual concentration from calculated one and subsequently the potential jumps occur at the new equivalence volume.

In back titration technique, for the standard Pt/SCE system, the height of jump increased in solutions as in the following order:  Cl$\ominus$ < I$\ominus$ < Br$\ominus$ while for Ta/SCE system, the order is: Br$\ominus$ < Cl$\ominus$ < I$\ominus$, for Ta/Pt is: Cl$\ominus$ < Br$\ominus$ < I$\ominus$ and for Ta/ Ag is: Cl$\ominus$ < Br$\ominus$ < I$\ominus$ (Table 2). In I$\ominus$ solution, the value of potential jumps increase with increasing halogen volume for all systems used. The highest jumps of Ta systems were observed in Ta/SCE followed by Ta/ Ag then Ta/ Pt system. For Br$\ominus$ and Cl$\ominus$ solutions, the value of potential jump increases with increasing halogen volume except for Ta/Ag and Ta/SCE systems respectively which behave reversibly. In this technique, and for all halogen solutions, the experimental end points coincide or state very close to the calculated end points (0.8, 1.2 and 2.4 ml for 1.5, 2.5 and 5 ml halogen solution).

From the above observations, the shape of the titration curves and the magnitude of potential jumps depend upon the kind of halogen, its concentration as well as on the particular coupled system used and type of titration when the experiment is carried out.

It is noteworthy to mention that, in precipitation titrations the efficiency of the electrode infrequently depended on the nature of the precipitate; the finer the precipitate, the less likely is the electrode to give satisfactory results.

The main application of the combined system described is for indication of the end-point in potentiometric titration of precipitation reactions. Electromotive force of the metallic combination electrode assembly dips in the solution of halogen investigated is given by Nernst equation:

$$E = E° - 0.0591 \log a_{X^-} \qquad (2)$$

Where, $X^-$ is the halogen ions concentration.

By using the above mentioned combinations, it is noted that, in forward titrations and before the equivalence point, the increase of electrode potentional responds to the change in halogen concentration as followed by equation (2). After the equivalence point, the system responds to the changes of $AgNO_3$ titrant. Any further addition of titrant causes further increase of electrode potential i.e. the titration curves obtained exhibit regular defined and sharp inflexion points with high potentional jumps at the equivalence point.

**Table (2): Comparison among different electrode systems in precipitation titration reactions for 0.1M halogen solutions**

| System | Vol. (ml) | 0.1N KI | | 0.1N KBr | | 0.1N KCl | |
|---|---|---|---|---|---|---|---|
| | | Equivalence Vol., (ml) | Jump height, mV | Equivalence Vol., ml | Jump height, mV | Equivalence Vol., ml | Jump height, mV |
| **Forward** | | | | | | | |
| Pt/SCE | 1.5 | 2.5 | 253 | 2.5 | 367 | 7.5 | 236 |
| | 2.5 | 3.5 | 372 | 4.3 | 385 | 10.5 | 203 |
| | 5.0 | 8.0 | 350 | 9.0 | 378 | 25.3 | 250 |
| Ta/SCE | 1.5 | 2.5 | 689 | 2.5 | 699 | 7.5 | 352 |
| | 2.5 | 4.5 | 749 | 4.5 | 764 | 12.5 | 263 |
| | 5.0 | 8.5 | 716 | 8.5 | 728 | 24.5 | 240 |
| Ta/Pt | 1.5 | 2.5 | 613 | 2.5 | 363 | 8.5 | 52 |
| | 2.5 | 5.0 | 631 | 4.5 | 341 | 13.0 | 299 |
| | 5.0 | 9.0 | 537 | 8.5 | 262 | 25.0 | 138 |
| Ta/Ag | 1.5 | 3.0 | 101 | 2.5 | 361 | 8.5 | 40 |
| | 2.5 | 3.5 | 105 | 7.0 | 673 | 12.5 | 53 |
| | 5.0 | 8.5 | 148 | 9.5 | 452 | 13.5 | 25 |
| **Backward** | | | | | | | |
| Pt/SCE | 1.5 | 0.8 | 273 | 0.9 | 344 | 1.1 | 153 |
| | 2.5 | 1.5 | 277 | 1.7 | 352 | 1.6 | 203 |
| | 5.0 | 3.0 | 294 | 2.9 | 379 | 3.1 | 174 |
| Ta/SCE | 1.5 | 0.9 | 592 | 0.9 | 228 | 0.9 | 266 |
| | 2.5 | 1.5 | 599 | 1.2 | 231 | 1.7 | 261 |
| | 5.0 | 3.1 | 608 | 2.7 | 246 | 3.4 | 241 |
| Ta/Pt | 1.5 | 0.9 | 247 | 0.9 | 227 | 1.3 | 88 |
| | 2.5 | 1.5 | 270 | 1.3 | 257 | 1.7 | 95 |
| | 5.0 | 3.2 | 369 | 2.7 | 293 | 3.4 | 158 |
| Ta/Ag | 1.5 | 1.1 | 351 | 1.0 | 297 | 1.0 | 70 |
| | 2.5 | 1.6 | 373 | 1.4 | 282 | 1.6 | 114 |
| | 5.0 | 3.0 | 473 | 2.6 | 272 | 3.2 | 117 |

## Conclusion

From the analytical point of view which is the object of this investigation, the following arguments can be drawn: In precipitation titrations, using Ta/SCE, Ta/Pt and Ta/Ag systems for Cl$^{\ominus}$, Br$^{\ominus}$ and I$^{\ominus}$ solutions against AgNO$_3$ solution and avoiding the diffusion of Cl$^{\ominus}$ ions from the salt bridge, the end point is signified by a sharp jump in potential or by the presence of a potential peak at the equivalence volume.

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