Applicability of Molybdenum Electrode as an Indicator Electrode in Potentiometric Titration of Simple and Polyelectrolytes

M.M.B. EL-SABBAH, M.E. IBRAHIM, R.M. ABU-SHAHBA, N.S. MOHAMAD AND A.A.ABDELLAH

Chemistry Department, Facultry of Science, Al-Azhar University Nasr City, Cairo, Egypt

A number of strong and weak, mono, and polybasic acids were potentiometrically titrated against standard solutions of NaOH and NH_4OH successfully using Molybdenum as indicator electrode. Mo/SCE combination was found to be as good as glass electrode/SCE or Pt/SCE Combination.

Indicator electrodes should satisfy certain requirements depending upon the reaction to be tested. In neutralization reactions, e.g. the electrode should be both acid and alkali resistant, and respond linearly to variations in pH[1]. The glass electrode[2] and a large number of metal-metal oxide electrodes[2] are commonly used. Many combination of number of metals with platinum have been studied [3,4]

The aim of this investigation is to establish the feasibility of (i) Mo as indicator with SCE as a reference electrode (ii) Pt/Mo bimetallic combination in potentiometric titrations.

EXPERIMENTAL

Spectroscopically pure Mo rods were cut, welded to thick Cu wires and mounted in pyrex-glass tubings in a manner that the weldings being isolated and an area of about 2.5 cm^2 could be exposed to the solution. Before each experiment, the electrode was abraded successively to the finest grade emery paper, degreased with acetone, washed with bidistilled water and dried between two filter papers. The titration vessel was a 100 ml pyrex-glass beaker. The Mo, Pt, glass and Calomel electrodes were fixed in a rubber stopper with four openings and placed over the titration cell such that they can be dipped into the solution easily. The titrations were carried out at 25±1°C using pH-mV potentiometer.

All chemicals used were of A.R. quality and were used without further purification. Doubly ditilled water was used in the preparation of the solutions. All solutions were prepared and standardised according to recommended procedures[5]

The polyelectrolyte prepared as described elsewhere[6] from the condensation of poly(vinyl alcohol) and mono-chloroacetic acid.

A titration of typical strong and weak mono-and polybasic acids. [HCl, HCOOH, $H_2C_2O_4$, H_3PO_4 and polyelectrolyte] with NaOH and NH_4OH were carried out with Mo electrode. Both acid titration with alkali and the reverse titrations were carried out. The potential of the Mo electrode relative to SCE, was measured, during the course of titration. For the sake of comparison, the titrations were followed simultaneously with either a glass electrode or Pt-electrode, and the change of pH was recorded The potential of Mo/Pt combinations was also measured In each experiment, the indicator electrode was left in the solution to be titrated till the establishment of the steady state potential. During titration, potentials were measured 5 minutes after each addition of the titrant so that a steady potential could be recorded. Each titration experiment was repeated several times to ensure reproducibility.

Potentiometric titration of polyelectrolyte: A weighed amount of the polymer (1.5 gm/10 ml deionized water) in the H-form was titrated using sodium hydroxide solution with vigorous stirring. The constant pH value reached, was measured 30 mins after each addition with the help of glass/SCE and Mo/SCE electrodes (at 25°C±1).

The same experiment was carried out under the same conditions, when the polymer was dissolved in aqueous potassium chloride solutions of different concentrations (0.1, 1.0 and 2.0 M).

RESULTS AND DISCUSSION

Mo ELECTRODE AS AN INDICATOR ELECTRODE IN ACID-BASE TITRATION:

Figs. (1-4) represent typical titration curves of the titration of 0.1N solutions of HCl, $H_2C_2O_4$, HCOOH and H_3PO_4 acids with 0.1N NaOH with Mo electrode. Fig. (5) represent the titration of 0.1 N HCl with 0.1 N NH_4OH Curves (B) of the same figure represent the backward titrations of the same solutions, using the same electrodes.

The potential of the Mo electrode is negative w.r. to SCE in the entire titration range, becoming more negative with increase in pH. Titration curves of strong acid-base titrations are characterized by a single potential inflection of about

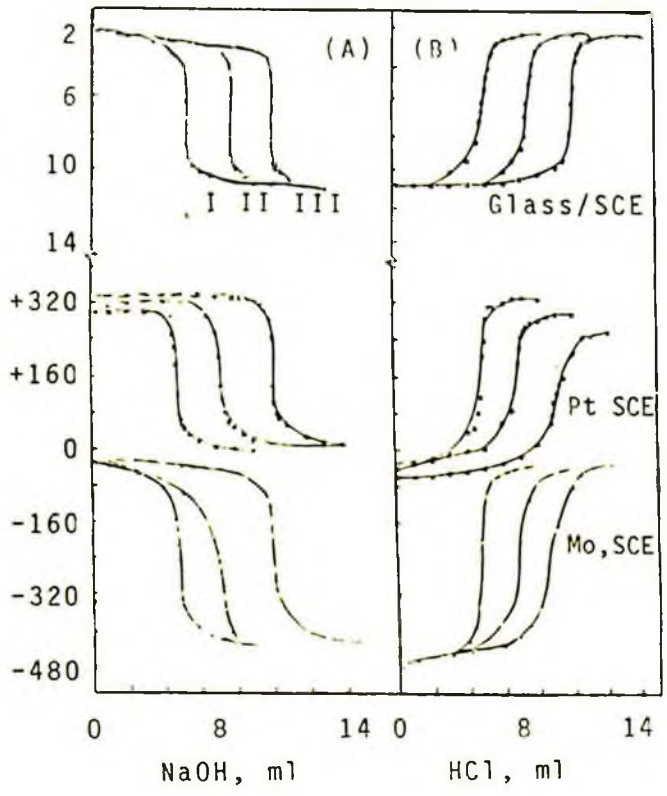


Fig. 1 Forward (A) and Backward (B) Titration Curves of 5(I), 7.5 (II) and 10 (III) ml of 0.010N HCl solution with 0.094N NaOH solution.

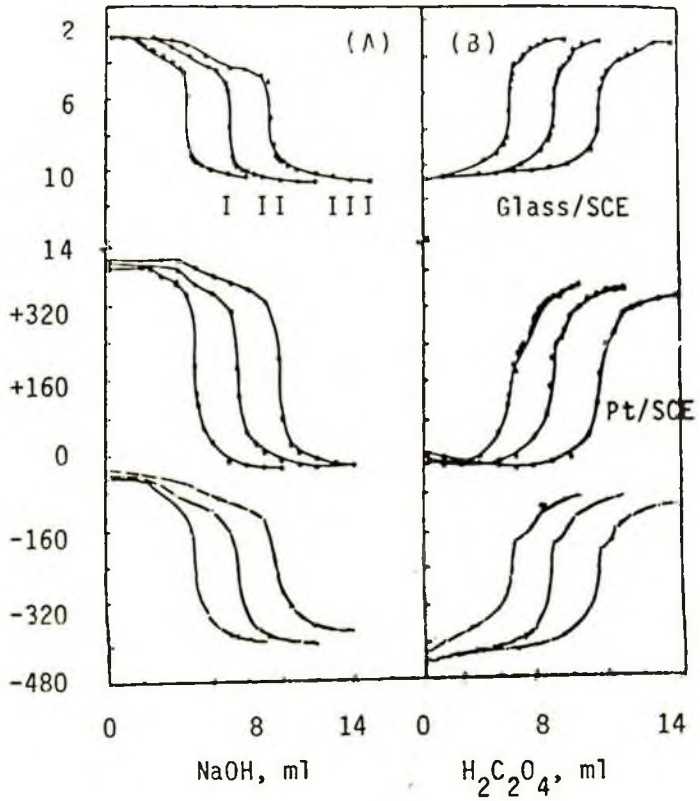


Fig. 2 Forward (A) and Backward (B) Titration Curves of 5 (I), 7.5 (II) and 10 (III) ml of 0.1N $H_2C_2O_4$ solution with 0.099N NaOH solution.

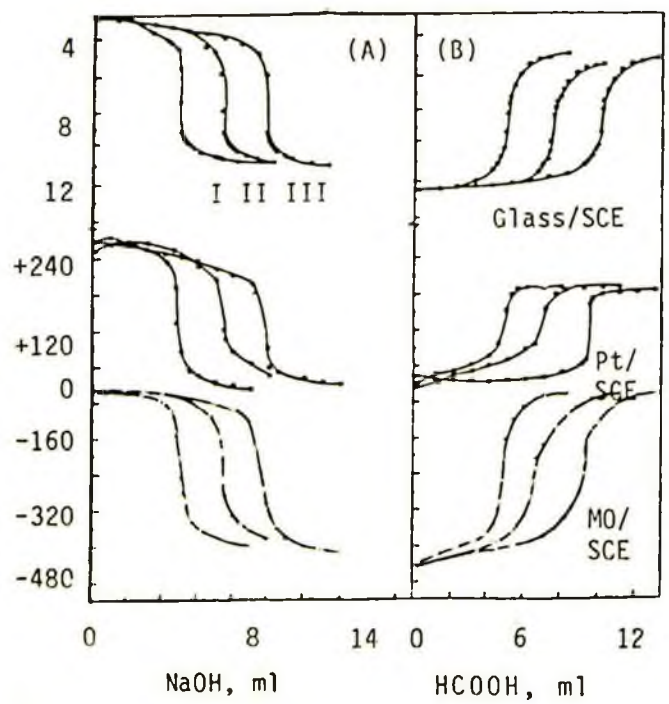


Fig. 3 Forward (A) and Backward (B) Titration Curves of 5 (I), 7.5 (II) and 10 (III) ml of 0.098N HCOOH solution with 0.098N NaOH solution.

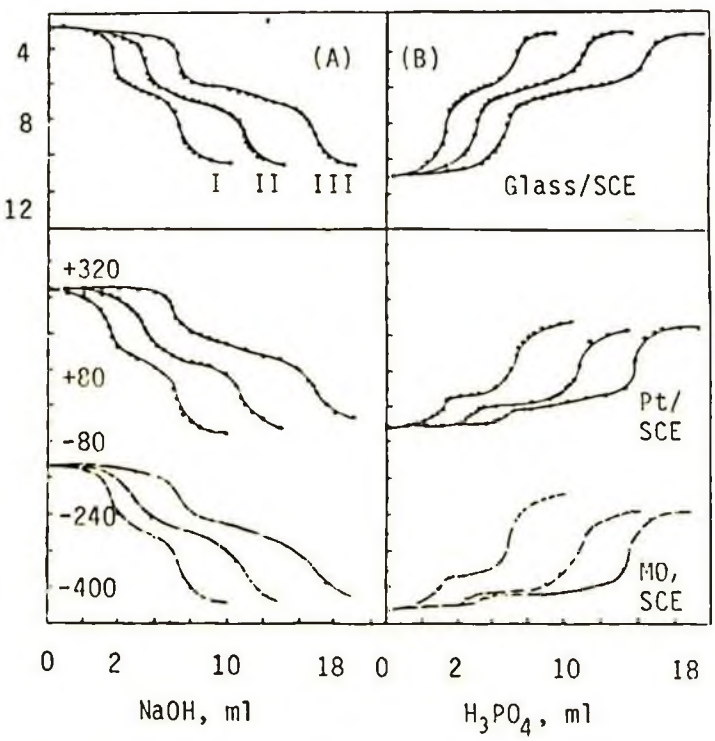


Fig. 4 Forward (A) and Backward (B) Titration Curves of 5 (I), 7.5 (II) and 10 (III) ml of 0.066M H_3PO_4 solution with 0.101M NaOH solution.

300 mV, at the equivalence point. This inflexion coincides with that obtained with Pt/SCE. In the case of formic acid the value of potential inflexion is smaller than the corresponding one obtained with HCl, Table 1. This is attributed to the higher pK_a value of formic acid.

TABLE 1

COMPARISON OF DIFFERENT ELECTRODE SYSTEMS IN AQUEOUS ACID BASE TITRATIONS: REFERENCE ELECTRODE IS SCE IN ALL CASES

Acid	Base	pH electrode	Curve height mV
HCl	NaOH	Glass	- 9 (a)
		pt	300
		Mo	350
H_3PO_4	NaOH	Glass	- 8.5(a)
		pt	240
		Mo	240
HCOOH	NaOH	Glass	- 8 (a)
		pt	200
		Mo	250
$(COOH)_2$	NaOH	Glass	- 8 (a)
		pt	240
		Mo	240
HCl	NH_4OH	Glass	- 7 (a)
		pt	300
		Mo	300

Oxalic acid is a dibasic acid with $K_1 = 5.3\times10^{-2}$ and $K_2 = 5.3\times10^{-5}$ (10) but only one neutralization step is clearly measured (Fig.2) This step corresponds to 2 mole NaOH/1 acid, which reflects the failure of Mo electrode to separate the two neutralization steps.

Titration curves of H_3PO_4 with NaOH using Mo as indicator electrode are characterized by two potential inflections,

(a) pH units

Fig. (4). The uptake of the titrants along each of the steps is equal and corresponds to 1 mole NaOH/1 mole H_3PO_4, representing the successive formation of mono, and dibasic salts according to:

$$H_3PO_4 + OH^- = H_2PO_4^- + H_2O \quad \ldots\ldots\ldots (1)$$

This is as expected because of the marked difference between K_1 and K_2 of H_3PO_4, [7.5×10^{-3} and 6.2×10^{-8}] no inflection is recorded corresponding to the third ionization due to the very low value of K_3 for H_3PO_4 (5×10^{-13}).

This potential difference Mo/Pt bimetalic combination remains constant along the major part of the titration curve. A small peak at the equivalence point is easily missed, so the use of Mo/Pt bimetallic electrodes is not recommeded in such reactions.

The suitability of the Mo electrode for the equation pK values of weak acids was also tested. Using the simplified Henderson-Hasselbach equation[7],

$$pH = pK_a + \log [salt]/[Acid] \quad \ldots\ldots\ldots (3)$$

[Salt] is the neutralized part of the [Acid] is the unneutralized part of the acid and pK_a is the classical dissociation constant since [salt] and [acid] are concentrations and not activities. Since the Mo electrode vary its potential at a rate of - 45 mV/pH unit[9] in air saturated solutions, the pH value corresponding to a certain Mo electrode potential can be calculated according to:

$$pH = (E - E_m)/ 0.045 \quad \ldots\ldots\ldots\ldots (4)$$

Where E_m is the measured potential and E is the interpolated potential of the electrode to pH = 0. Calculations were made for 25,50 and 75% neutralization of the second step of phosphoric acid and for the neutralization steps of both formic and oxalic acids. The pK values obtained are presented alongwith literature values in Table (2) for comparison

APPLICABILITY OF MO-ELECTRODE AS AN INDICATOR ELECTRODE IN POTENTIOMETRIC TITRATION OF POLYELECTROLYTE :

Potentiometric titration curves can be made use of to evaluate pK values and weight exchange capacitites of polyelectrolytes. Sharp end points and precise titrations are reached if small amounts of neutral salt are added[10]

Titrations were carried out using 10 ml of 15% solutions of the prepared polyelectrolyte in deionized water as well as in solutions of different KCl concentrations. Titrant was 0.445 M NaOH. Mo electrode was used as an indicator electrode. The titration curves are represented by the curves of Fig. (6). These titrations are repeated using glass electrode. The weight exchange capacities of the polyelectrolyte in different media was computed from the amount of

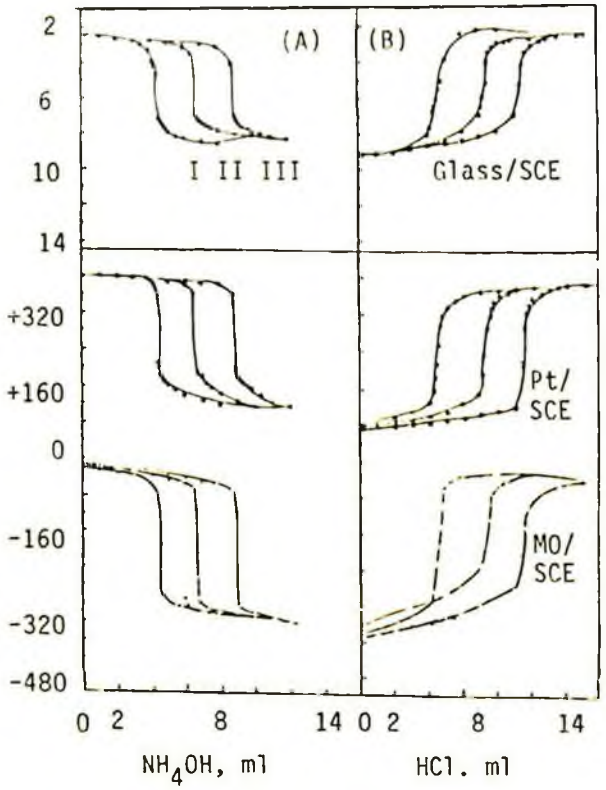


Fig. 5 Forward (A) and Backward (B) Titration Curves of 5 (I), 7.5 (II) and 10 (III)ml of 0.102N HCl solution with 0.1145N NH_4OH solution.

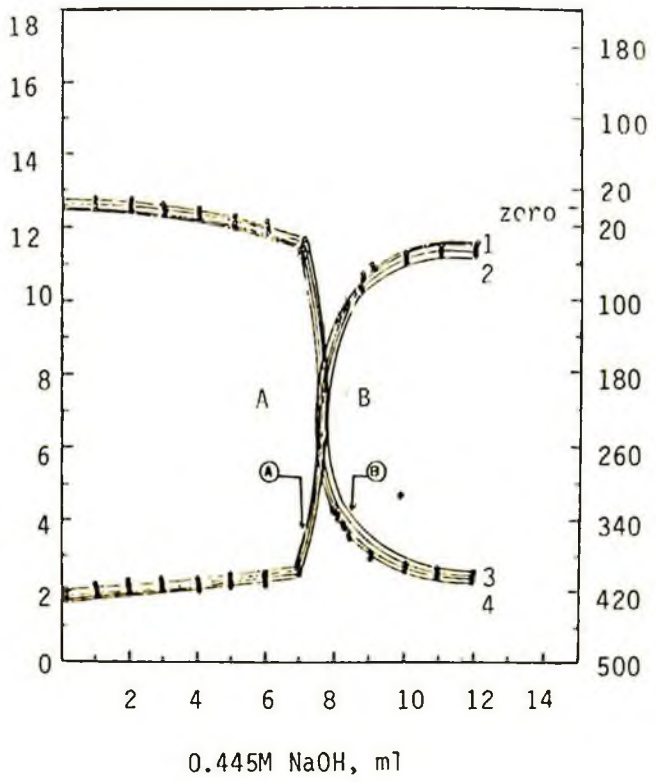


Fig. 6 Potentiometric Titration Curves for the Polyelectrolyte using various Electrodes:-

(A) Glass/SCE
(B) MO/SCE.

(1) In Deionized Water
(2) In 0.1M KCl Solution.
(3) In 1.0M KCl Solution.
(4) In 2.0M KCl Solution.

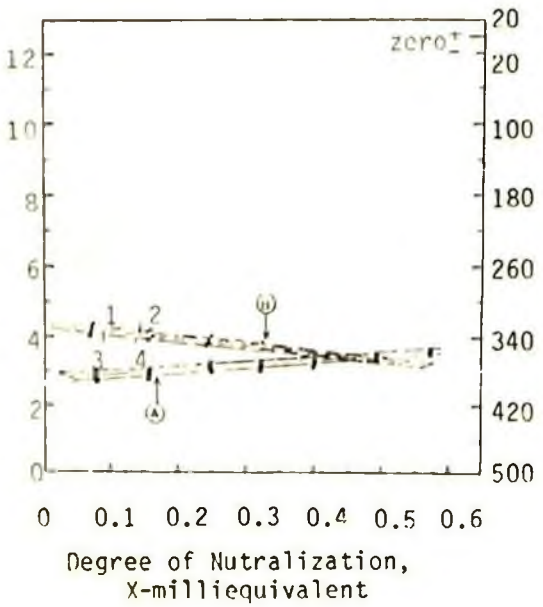


Fig. 7 (A) Plots of pH + log $[1-x/x]$ against x for Glass/SCE system.

(B) Plots of $\frac{E-E_m}{0.045}$ + log $\frac{1-X}{X}$ against x for Mo/SCE system.

(1) In Deionized Water.
(2) In 0.1M KCl solution.
(3) In 1.0M KCl solution.
(4) In 2.0M KCl solution.

TABLE 2

Acid or Base	System	Mean pK	pK
Acid			
HCOOH	Glass/SCE	3.77	3.75
	Mo/SCE	3.80	
$(COOH)_2$	Glass/SCE	4.22	4.19
	Mo/SCE	4.16	
1st step of H_3PO_4	Glass/SCE	2.15	2.12
	Mo/SCE	2.18	
2nd step of H_3PO_4	Glass/SCE	7.29	7.21
	Mo/SCE	2.18	
Base			
NH_4OH	Glass/SCE	4.78	4.75
	Mo/SCE	4.81	

titrant required to bring the pH = 7 (using glass electrode) or to bring the potential to - 220mV (using Mo/SCE) Calculated weight excahnge capacities are listed in Table 3. It is clear that the two sets of vlaues are in quite agreement and the maximum deviation does not exceed 10% from the published data[11].

TABLE 3

Medium	Weight exchange capacities (meq./g) Glass	Mo	Published[11]
Deeionized water	2.352	2.252	2.461
0.1M KCl soln.	2.448	2.348	2.655
1.0M KCl soln.	2.511	2.511	2.867
2.0M KCl soln.	2.712	2.712	3.033

It was observed that for Mo/SCE combination plots of E vs ml of titrant gives a well defined titration curve (fig 6). Mo electrode can be used as an indicator electrode in titration of electrolytes also. Henderson-Hasselbach equation can be written in the form $pH = pK + n \log \frac{[x]}{[1-x]}$ where x is the fraction of acid neutralized using Mo/SCE electrodes

Plots of $\frac{E-E_m}{0.045} + \log \frac{1-X}{X}$ vs x (Fig 7) give straight lines.pK values are calculated and presented in Table 4

TABLE 4

Medium	Apparent pK-values Glass/SCE pK	Mo/SCE pK	Published[11]
Deionised water	3.80	3.8	3.8
0.1 M KCl soln.	3.55	3.55	3.6
1.0 M KCl soln.	3.50	3.50	3.55
2.0 M KCl soln.	3.45	3.45	5.45

Hence pK values, of a number of inorganic groups and weight excahnge capacities computed from the results obtained by this electrode are in quite agreement with those obtained by the universal glass electrode and the previously reported data.

REFERENCES

1. M.M.B. El-Sabbath, M.E. Ibrahim, and R.M. Abu-Shahba, Ind. Chem. Soc. submitted.
2. H.T.S. Britton, "Hydrogen Ions" Vol. 1, Chapman and Hall, (1955) p. 96,113.
3. N.H. Furman; J. Am. Chem. Soc., 50, (1928) 273, 277
4. I.M. Kolthoff,; Anal. Chem., 26 (1954) 1689
5. S. Vogel "Textbook of quantitative Inorganic Analysis", ELBS Longman (1978) P-600
6. E.A. Hassan, and M.M.B. El-Sabbah, Egypt J. Chem. No.4, (1974), 489/498.
7. M.L. Miller, "The structure of polymers", Reinhold Book Corporation, New York (1966) p 580-651.
8. P. Helfferish, "Ion-Exchange", McCraw-Hill (1962) 74.
9. Hand book of chemistry and physics, (CRC press), Inc. Cleveland, Ohio (1974-1975).
10. H.F. Mark, N.G. Gaylord, N.M. Bikales, Encyclopedia of polymer Sciences and Technology, Vol.1, Interscience Publishers, New york, np. 212 (1964).
11. E.A. Hassan, and M.M.B. El-Sabbah, Egypt J. Chem. 17, No. 6, 907-10 (1974).

PRECIOUS METAL PRODUCTS FOR ELECTROCHEMICAL APPLICATIONS

1. RUTHENIUM TRICHLORIDE, $RuCl_3 . 3H_2O$
   IRIDIUM TRICHLORIDE, $IrCl_3 . 3H_2O$

   — used for coating TITANIUM STABILISED INSOLUBLE ANODES for chlor-alkali industry.

2. SILVER CHLORIDE blanks sheets
   — used for making sea water batteries.

3. Platinum anodes in various forms—

   Platinum clad copper rods, foils etc. for Chlorate industry and various electrochemical applications.

4. Continuous cast Silver anodes to desired dimensions.

5. Plating salts and solutions —

   Potassium Gold Cyanide
   Gold Plating salt 40%
   Palladium Plating Salt.
   Platinum Plating Salt.
   Rhodium Plating Solution.

6. Silver Oxide to rigid specifications for button cells manufacture.

7. Silver Powder and foils for Silver/Zinc Oxide batteries.

MANUFACTURED BY :

Telegram : Platmetals, Regent Park, Calcutta-700 040

Telephones : Office 72-1207
.. 72-1799
Works 72-1798
City off. 34-9753

Telex : 021-2393 AML IN

ARORA MATTHEY LIMITED

Associates of : JOHNSON, MATTHEY PUBLIC LIMITED COMPANY, LONDON

MANUFACTURERS IN PRECIOUS METALS

(Compounds Apparatus Alloys Contacts Catalysts Fabrications)

Registered Office & Works : 166, NETAJI SUBHAS CHANDRA BOSE ROAD, TOLLYGUNGE, CALCUTTA-700 040, INDIA