CHEMICAL OSCILLATIONS IN Mn²⁺ CATALYSED BELOUSOV-ZHABOTINSKII AND DEPENDENCE OF TIME OF INITIATION AND TIME PERIOD OF OSCILLATIONS ON BROMIDE ION CONCENTRATION

THE oscillatory reaction between malonic acid, bromate and cerous ions in sulphuric acid medium has recently been extensively studied[1]. The role of Br^- is crucial for this reaction[2-5]. A study of dependence of oscillatory characteristics like time of initiation, t_{in} and time period, t_0 of oscillations on $[Br^-]$ will help in understanding the mechanism of the reaction and hence the present investigation was undertaken.
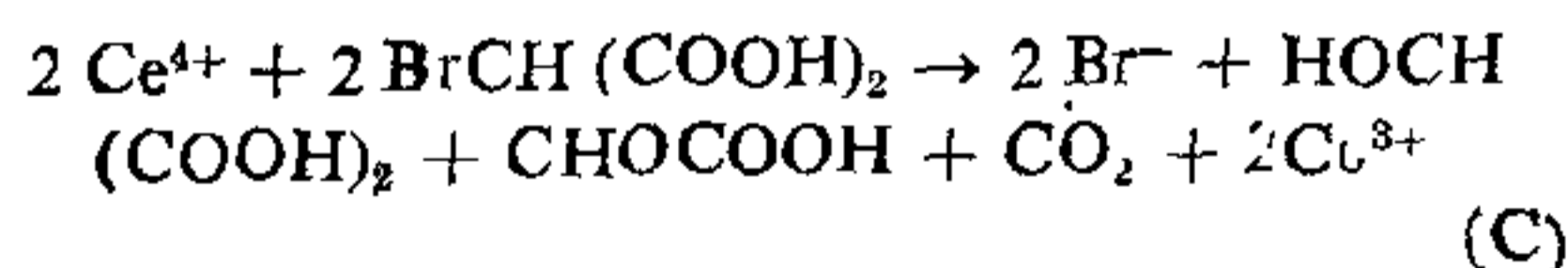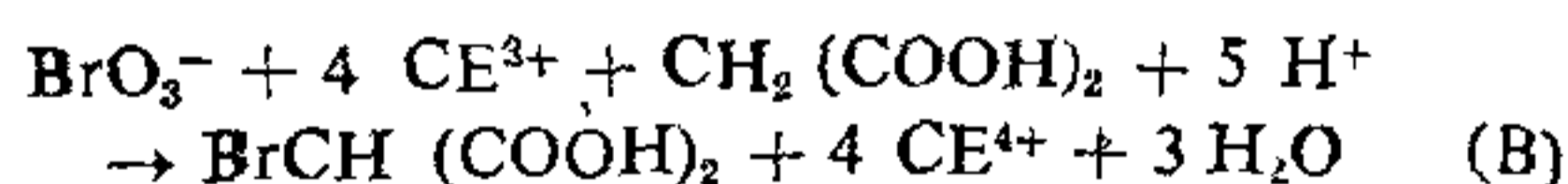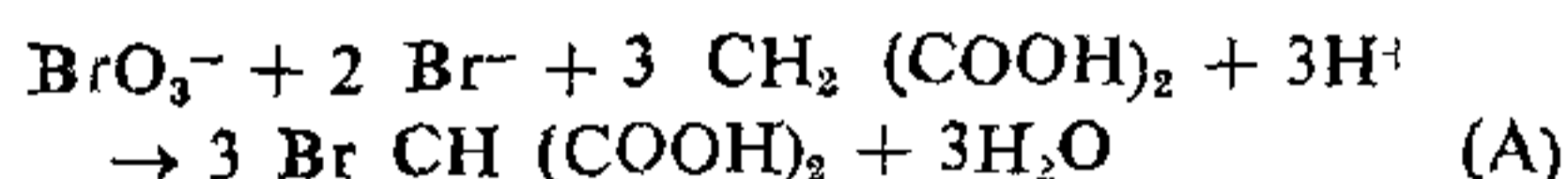
Chemicals used were of A. R quality.

Procedure

To a solution containing malonic acid (MA), manganous sulphate and potassium bromide in sulphuric acid equilibrated at $40 \cdot 0 \pm 0 \cdot 05°C$ was added potassium bromate solution, at the same temperature. The reaction was followed potentiometrically using a bright Pt wire indicator electrode coupled with a reference S.C.E. through agar-agar/potassium sulphate salt bridge. The e.m.f. of the system was recorded with time. It initially decreased followed by a sudden rise signalling the onset of oscillatory state. The time elapsed between mixing all the components of the reaction and the onset of oscillatory state is referred to as time of initiation of oscillation, t_{in}. The time interval between two minima in the e.m.f. vs. time plot gives the time period of oscillations, t_0. The mean of the first five time periods was taken. Results are plotted in Fig. 1.

Discussion

Noyes and coworkers[2-5] proposed a mechanism (FKN) involving the reaction sequence (A), (B) and (C) :

$$BrO_3^- + 2\ Br^- + 3\ CH_2\ (COOH)_2 + 3H^+$$
$$\rightarrow 3\ Br\ CH\ (COOH)_2 + 3H_2O \qquad (A)$$

$$BrO_3^- + 4\ CE^{3+} + CH_2\ (COOH)_2 + 5\ H^+$$
$$\rightarrow BrCH\ (COOH)_2 + 4\ CE^{4+} + 3\ H_2O \qquad (B)$$

$$2\ Ce^{4+} + 2\ BrCH\ (COOH)_2 \rightarrow 2\ Br^- + HOCH$$
$$(COOH)_2 + CHOCOOH + CO_2 + 2Ce^{3+} \qquad (C)$$

Reaction (A) occurs in presence of excess of Br^- and consists of reactions $(R_3) + (R_2) + (3\ R_1) + (3\ R_8)$

$$BrO_3^- + Br^- + H^+ \rightarrow HBrO_2 + HOBr \qquad (R_3)$$

$$HBrO_2 + Br^- + H^+ \rightarrow 2\ HOBr \qquad (R_2)$$

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \qquad (R_1)$$

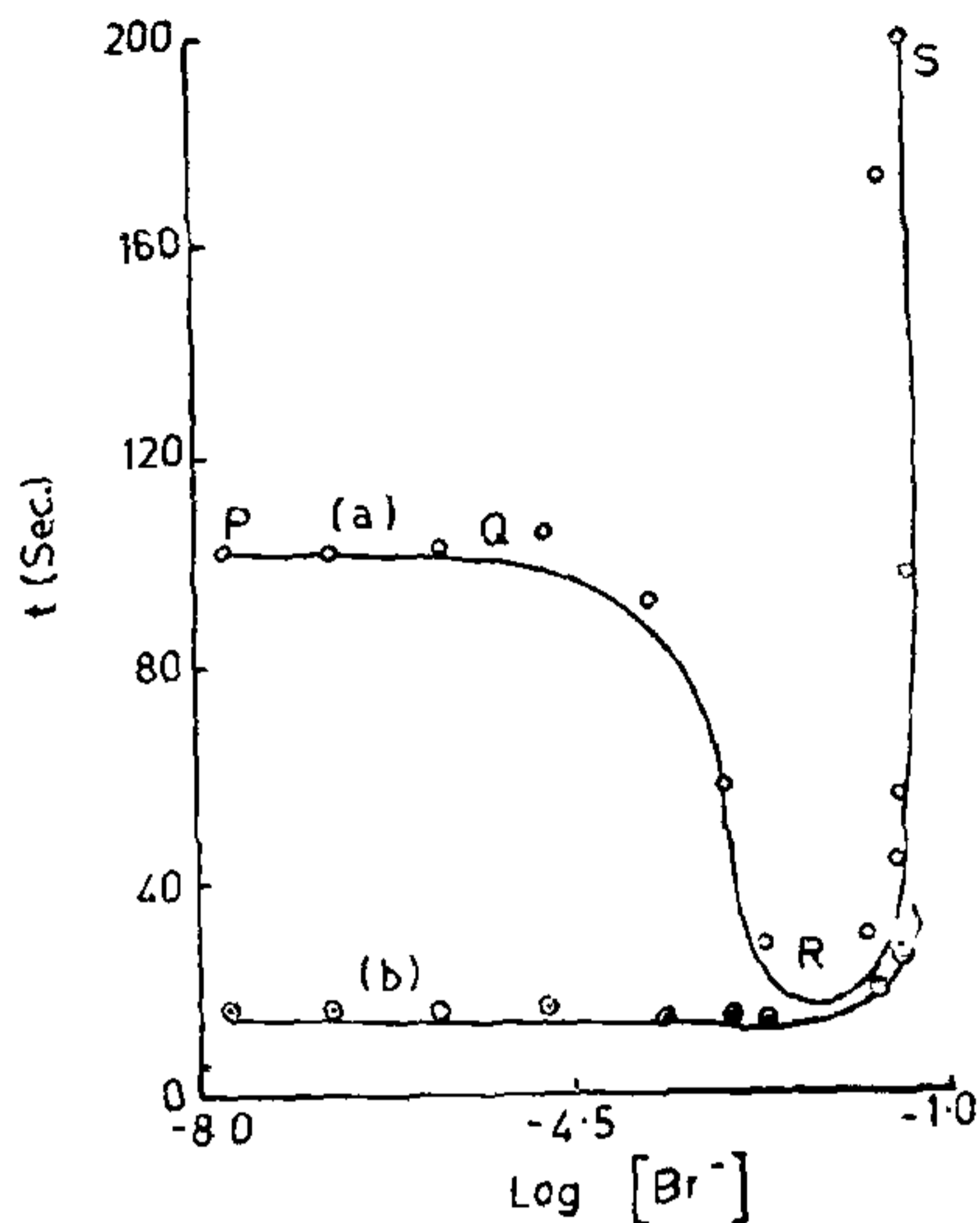$$Br_2 + CH_2\ (COOH)_2 \rightarrow BrCH\ (COOH)_2$$
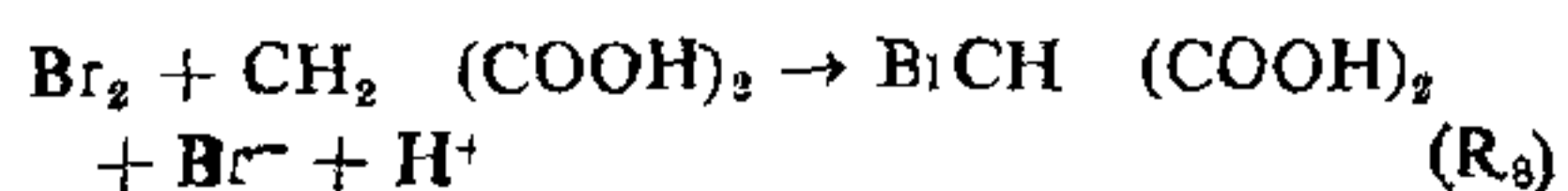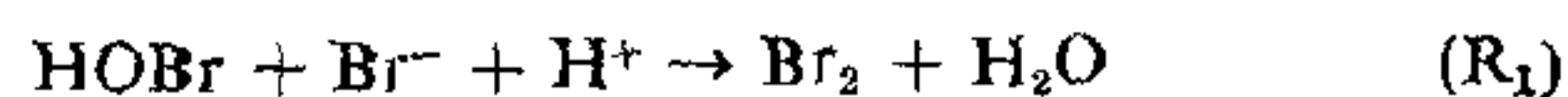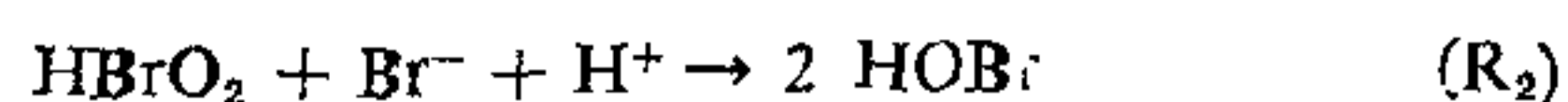$$+ Br^- + H^+ \qquad (R_8)$$

FIG. 1. Dependence of time of initiation of oscillation, t_{in} and time period of oscillations, t_0, on potassium bromide concentration

(Malonic aicd) $= 0 \cdot 064$ M, (KBrO₃)) $= 0 \cdot 044$ M
(MnSO₄) $= 0 \cdot 0008$ M, (H₂SO₄) $= 1 \cdot 0$ M
Temperature $= 40 \cdot 0° \pm 0 \cdot 05°$ C

Reaction (B) occurs due to reactions $(2R_5) + (4R_6) + (R_4) + (R_8)$ where $(R_5) + (2\ R_6)$ leads to the autocatalystic production of $HBrO_2$.

$$BrO_3^- + HBrO_2 + H^+ \rightarrow 2\ BrO_2 \cdot + H_2O \qquad (R_5)$$

$$BrO_2 \cdot + Ce^{3+} + H^+ \rightarrow HBrO_2 + Ce^{4+} \qquad (R_6)$$

$$2\ HBrO_2 \rightarrow BrO_3^- + HOBr + H^+ \qquad (R_4)$$

Autocatalytic state ensures when $[Br^-]$ is reduced to a critical value due to reaction (A). There is an induction time between the depletion of Br^- to the critical value and the onset of oscillatory state. According to Field and Noyes[6] the system attains the oscillatory state when bromomalonic acid (BrMA) is formed to such an extent that the reduction of Ce^{4+} by MA and BrMA yields the ratio of $[Ce^{4+}]_{reacted}$ to $[Br^-]_{produced}$ between $0 \cdot 5$ to $1 \cdot 5$. Results shown in Fig. 1 (a) and (b) will now be analysed in the light of the above mechanism.

Fig. 1 (a) shows t_{in} to be independent of bromide ion concentration upto 10^{-4} M (PQ portion of the curve). On increasing the bromide ion concentration further, t_{in} decreases rapidly (portion Q R of the curve) facilitating the reactions leading to the onset of oscillations. The t_{in} shows a minimum at $[Br^-] \simeq 10^{-3}$ M beyond which it begins to increase. According to

the FKN mechanism the initial decrease of t_{in} by increasing [Br⁻] can be explained by the formation of $HBrO_2$ from the reduction of BrO_3^- by Br⁻ through step (R_3) of the mechanism followed by reactions $(R_5) + (R_6)$ leading to the autocatalytic state. However, when Br⁻ is in excess the overall reaction (A) results in grater concentration of BrMA. The FKN mechanism assumes a shortening of induction period if BrMA is added to the system[6]. Thus the increase of t_{in} with increase of (Br⁻) (portion RS of the curve) is not explained by the FKN mechanism. It seems Br⁻ formed by the oxidation of BrMA by Mn^{3+} inhibits the autocatalysis through (R_3).

With increase of bromide ion concentration the time period, t_0, remains constant till (Ir⁻) showing minimum t_{in} is reached. The t_0 may be assumed as the time interval between two consecutive utocatalytic states. The reaction steps intervening this period involves (i) the disproportionation of $HBrO_2$ forming Br_2 through $(R_4) + (R_1)$ followed by the bromination of malonic acid (R_3), (ii) oxidation of BrMA so formed by Ce^{4+} or Mn^{3+} ions liberating Br⁻ excess of which inhibits reaction (B) through reaction (R_2) and (iii) consumption of Br⁻ through (A) leading to its depletion followed by the onset of autocatalytic state. It seems with excess Br⁻ enough BrMA is formed which on further oxidation regenerates Br⁻. The greater amount of regenerated Br⁻ allows for greater inuction period when a longer steady state is obtaining between two competing reactions for $HBrO_2$, $(R_2) + (R_1)$ on one hand and $(R_5) + (R_6)$ on other.

No oscillation is observed when [Br⁻]/[BrO₃⁻] ⩾ 2. Major oscillations are not obtained when [Br⁻]/[BrO₃⁻] > 1. The first observation can be rationalised by the consumption of BrO_3^- due to the stoichiometry of reaction (A). When [Br⁻]/[BrO₃⁻] < 2 some BrO_3^- is available for further reaction.

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ON THE DEPOSITION OF MANGANESE AND OTHER METAL COMPOUNDS ON THE STONES IN RIVER BEDS

THERE has been considerable scientific[1,2] popular[3] and commercial interest, lately, on the metal compound deposits on the ocean floor. We have observed that deposits of metal compounds take place even on the river beds, in some selected areas. This observation was made on stones from some parts of river Tunga (a tributary of Tungabhadra, and of Krishna) at Sringeri, Karnataka State, India (13° 25' latitude, 75°15' longitude). We found that many of the stones were black in colour, only in certain areas of the river. Closer examination revealed that the black colour arose from superficial deposits of metal compounds on quartz pebbles. Qualitative analysis indicated that the stones themselves after leaching did not have manganese or iron. In Table I, are given the amounts of manganese and iron on the black stones picked up at random in the place of their abundance.

The stone samples were leached with aqua regia and the extracts were made up to known volumes and used for atomic absorption spectroscopic measurements. The values reported in Table I are the mean values of three measurements.

In Fig. 2 are plotted the amounts of the deposits of manganese and iron as a function of the surface area of the stones. Whereas a rough correlation exists between the surface area and the deposits of manganese on different stones, such a correlation was not found with iron. The Deposition of iron *versus* manganese on individual stones, plotted in Fig. 1 also shows no significant correlation.

In conclusion it can be stated that the deposits are purely superficial in nature. Manganese gets deposited on the surface of pebbles possibly because of microbiological activity at the time of deposition. The deposition of iron is random and could be from the suspended iron oxides and other iron compounds in water.