An EPR study of chemical oscillators

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We report the follow-up of the Briggs–Rauscher oscillatory reactions, not hitherto successful with the EPR technique, in this communication. The system includes, besides hydrogen peroxide, acidified iodate and manganous sulphate, diethyl malonate as the substrate. We show a comparison of the EMF and EPR profiles. The EPR technique would be highly suited for investigation of chemical oscillators under favourable circumstances.

SINCE the discovery of oscillatory behaviour of the iodate-hydrogen peroxide system in solution by Briggs and Rauscher (BR)[1], these chemical oscillators have been studied by EMF and spectrophotometry[2–5] techniques. A typical mixture of diethyl malonate (DEM), potassium iodate, sulphuric acid, hydrogen peroxide and manganous sulphate undergoes oscillations. Its study by EMF technique has been reported in a previous communication[5]. During oscillations, the concentration of Mn(II) is reduced with a simultaneous increase in Mn(III) concentration, followed by the reverse reaction. Since the solution contains Mn(II) ions (d^5, paramagnetic), EPR spectroscopy is the best technique to study the small changes that occur in Mn(II) concentration and study the oscillations. In this communication, we report the oscillations observed by EPR technique using DEM substrate.

It was earlier reported[6] that EPR data could not be obtained for an oscillatory system: malonic acid, sulphuric acid, hydrogen peroxide, potassium iodate and manganous sulphate. One of the reasons may be that the concentration of paramagnetic ion is below the sensitivity of the method. However, we have repeated the same experiment with different concentrations of the constituents, especially higher concentration of Mn(II) and observed the oscillations using EPR technique. The same system was also studied by the EMF technique. A detailed report on this system will be published later.

The EPR spectra were recorded using a Varian E-112 EPR spectrometer operating at X-band frequency (ν is around 9.4 GHz) having a 100 kHz field modulation and phase sensitive detection to obtain the first derivative signal. The solutions (without hydrogen peroxide) were taken in an Varian E-248 quartz aqueous cell and the EPR spectrum was recorded. The spectra consist of six lines [nuclear spin of Mn(II) is 5/2] with a g value very close to 2.004(2) and an hyperfine coupling constant of 94(4) gauss. These are typical values for a Mn(II) system[7]. To record the oscillations with EPR, the following proceedure was adopted: the central field was set at the top position of the first derivative peak of the first hyperfine line and the scan range was switched off. The spectra were recorded as a function of time, after the addition of hydrogen peroxide. The procedure for EMF measurements was described earlier[5].

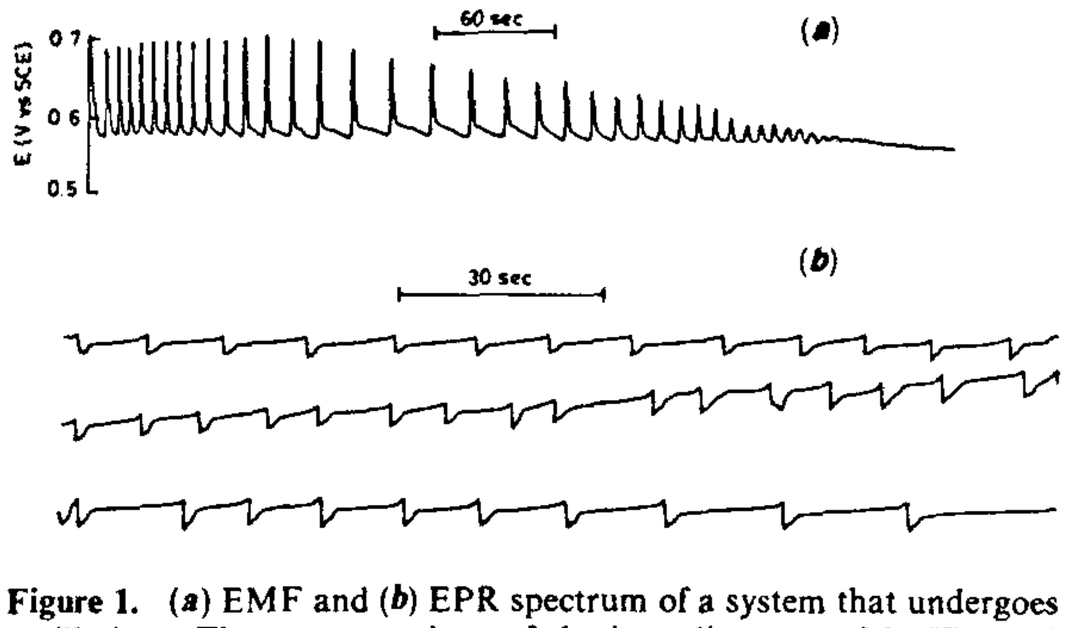

Figure 1. (*a*) EMF and (*b*) EPR spectrum of a system that undergoes oscillations. The concentrations of the ingredients are: Mn(II) = 0.02 M; DEM = 0.5 M; H_2SO_4 = 0.16 M; KIO_3 = 0.05 M; H_2O_2 = 1.2 M and acetonitrile (by volume) = 5%. The EPR spectrum was recorded at 25°C (ν = 9.45 GHz) and EMF at 28°C.

In this communication, we report the chemical oscillations observed in the system: DEM, KIO_3, H_2SO_4, H_2O_2 and $MnSO_4$, using EPR and EMF techniques. In a series of experiments, we have varied the concentrations of one of the constituents of the oscillatory system, by keeping the rest at constant values. The system contains 5% acetonitrile by volume. An EMF profile at noted concentrations of the ingredients is shown in Figure 1 along with the EPR spectrum recorded at the same concentrations. It is clear from this figure that the oscillations are not seen beyond 6.6 minutes in the EMF profile, whereas the oscillations are continued beyond 15 minutes in the EPR spectrum. This can be attributed to the higher sensitivity of the latter technique than the former. However, the number of oscillations obtained in 5 minutes is 25 and 28 respectively from these two techniques. This small difference is due to the difference in the temperature measurement[8] (EMF measured at 28°C, whereas EPR was at 25°C).

In Figure 1, the conversion of Mn(II) to Mn(III) is given by a sudden decrease in the intensity of the EPR signal, and an increase in Mn(II) is denoted by a sudden increase in the intensity of the signal. Similar results were also noticed in the EMF profile. As will be discussed in a future communication, if the retention of Mn(III) is higher than the present one (with a different substrate), a square wave type (⎍⎍⎍) is expected, and in fact observed in both the techniques. However, at this stage, it is difficult to conclude from the EPR spectrum the magnitude of the changes in concentrations of Mn(II) during oscillation.

Further work is in progress with other substrates

such as malonic acid, acetyl acetone, ethyl acetoacetate, etc.

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Radiocarbon dates of sediment cores from innercontinental shelf off Karwar, west coast of India

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Two samples of carbonized wood and one of shells from sediment cores off Karwar were dated by ^{14}C method. Radiometric ages of carbonized wood beds indicate transgression of the sea and submergence of coastal forests around 9000–10000 years before present in the Karwar area. The rate of sedimentation varies between 0.89 mm per year near the coast and 0.44 mm per year away from the coast.

PUBLISHED data on radiometric dates of marine sediments from western Indian continental shelf are far and few. This communication records radiocarbon dates of three samples, two of carbonized wood and one of shells, from three piston cores collected from the inner shelf off Karwar (Figure 1) on board *R V Samudra Shaudhikama.* The samples were dated at the Radiocarbon Dating Laboratory of the Birbal Sahni Institute of Palaeobotany, Lucknow, using the pre-treatment, chemistry and radioactive-counting procedures described elsewhere[1]. The significance of the age data in interpreting the Holocene history of the area is briefly mentioned here.

The carbonized wood dated occurs as a 18-cm-thick bed at a depth of 420 cm below seabed in PC-1464 (14° 25′ 37.091″ N 74° 12′ 35.501″ E). In PC-1490 (14° 40′ 8.631″ N 73° 59′ 9.568″ E), it occurs as a 2-cm-thick zone at a depth of 578 cm. A shell zone

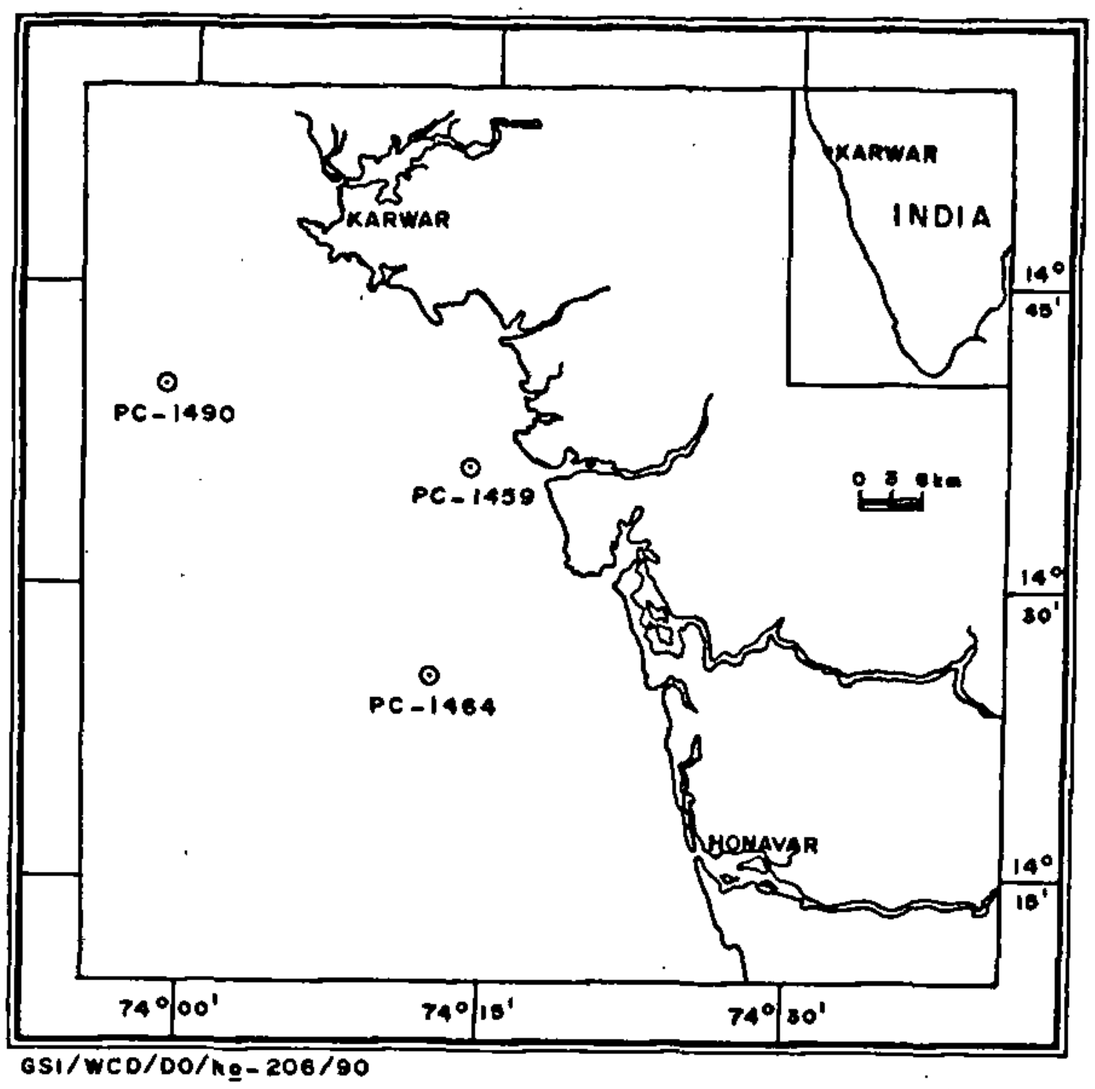

Figure 1. Location of the piston cores collected.

comprising broken and whole shells of lamellibranchs and gastropods occurs at a depth of 302 cm in core PC-1459 (14° 35′ 59.331″ N 74° 13′ 49.744″ E) and has been dated (Figure 2).

The radiocarbon dates of the samples are given below.

Sample	Material dated	Depth (cm)	Age (yr BP)
PC-1459/10	Shells	302–310	3410 ± 90
PC-1464/22	Carbonized wood	420–438	9630 ± 120
PC-1490/16	Carbonized wood	578–580	8620 ± 300

Occurrence of carbonized wood/peat beds associated with Recent sediments has been reported from many onshore and offshore areas of the west coast of India.

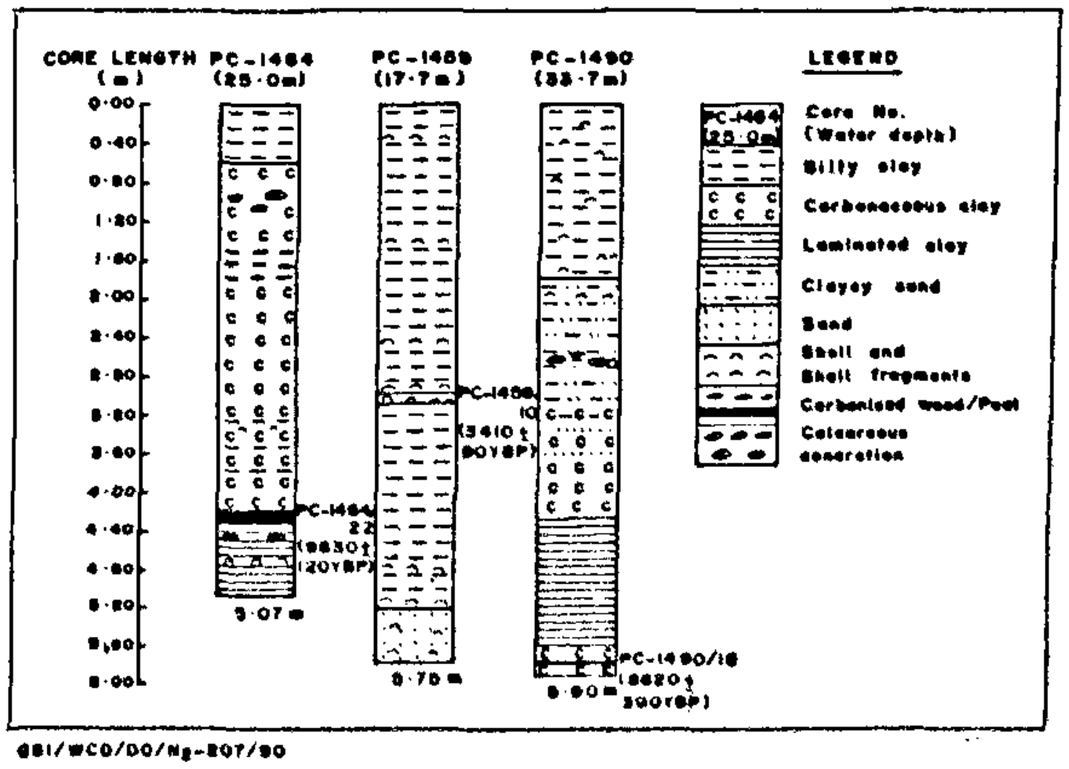

Figure 2. Lithology of the cores, with location of the samples dated.