

NQR frequency in these two solids both at 77 K and at room temperature. Two resonance lines have been observed in 2,4-dichlorobenzoic acid due to chemically inequivalent sites.

The resonance frequency of 5-amino-2-chlorobenzotrifluoride is higher than that of 2-amino-5-chlorobenzotrifluoride. This may be explained by the fact that chlorine occupying the ortho position will have a higher resonance frequency when compared to the chlorine occupying the meta position (Nagarajan and Murthy<sup>3</sup>). Similarly, when the resonance frequency of 4-chloro-2-nitrobenzoic acid is compared with that of 4-chloro-3-nitrobenzoic acid (37.483 MHz—Bray and Barnes<sup>2</sup>) and 4-chlorobenzoic acid (34.673 MHz—Meal<sup>4</sup>), we observe that the introduction of nitro group increases the resonance frequency. Also, 4-chloro-3-nitrobenzoic acid has a higher resonance frequency than 4-chloro-2-nitrobenzoic acid. This is because when the chlorine occupies the ortho position with respect to the nitro group a higher resonance frequency will result as compared with the chlorine in the meta position (Ref. 3).

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#### IN-SITU MEASUREMENT IS A MUST FOR SIZE EFFECT STUDIES OF THIN METAL FILMS\*

THE anomalous behaviour of the size dependence of the electrical transport properties in metals, semi-metals, semiconductors, alloys etc., may be associated with the anomalous conditions in the structure of thin films which should depend very much on the method and environment of deposition. So the experimental conditions should be the same as those which have been postulated when deriving relations in the theory of size effects (Fuchs<sup>1</sup>, Sondheimer<sup>2</sup>). It has been

observed (Garcia *et al.*<sup>3</sup>) that the film properties change drastically when the film is removed from high vacuum. So according to them, for accurate results the measurements should be done without removing the film from the high vacuum (*i.e.*, *in-situ*). Here the resistivity values for each of silver and copper films measured under *in-situ* and not *in-situ* conditions and deposited under extremely controlled evaporation conditions have been reported. In an earlier paper (Pal *et al.*<sup>4</sup>) we have reported the *in-situ* measurements of resistivity of silver films (300 Å to 2000 Å) at room temperature. In the present paper, the resistivity ( $\rho$ ) of the silver films is discussed as a function of thickness ( $t$ ) of the film at 30°C by keeping the films both inside (*in-situ*) and outside (not *in-situ*) the high vacuum (Fig. 1). The resistivity of the films was found to increase drastically, especially for the thinner ones when they were removed from high vacuum. Thinner films are affected more.

In the present paper, the effect of residual atmosphere on copper films has been studied at room temperature (Fig. 2) by exposing a thin copper film (thickness = 300 Å) prepared at a pressure  $1.33 \times 10^{-3}$  Newton/metre<sup>2</sup> to  $1.33$  Newton/metre<sup>2</sup>,  $1.33 \times 10^2$  Newton/metre<sup>2</sup> and  $1.013 \times 10^5$  Newton/metre<sup>2</sup> (*i.e.*, atmospheric) pressure by admitting air slowly. The method of preparation of the copper films was discussed in our earlier paper (Pal *et al.*<sup>5</sup>). From  $1.33 \times 10^{-3}$  Newton/metre<sup>2</sup> to  $1.33$  Newton/metre<sup>2</sup> pressure, there is practically no change in the resistivity  $\rho$  of the copper film. The resistivity very slowly changes up to  $1.33 \times 10^2$  Newton/metre<sup>2</sup> and finally increases abruptly as the film is exposed to atmospheric pressure. This change is very fast and the film stabilises within a few seconds. Even after annealing the previously exposed film at 120°C for about two hours at  $1.33 \times 10^{-3}$  Newton/metre<sup>2</sup>, the resistivity value remained 25% higher than that obtained with the fresh sample at  $1.33 \times 10^{-3}$  Newton/metre<sup>2</sup>. Murgulesch and Ionescu<sup>6</sup> also observed a change of 6% to 16% in the resistivity value of continuous copper films owing to adsorption of oxygen. Thus it may be concluded that one should make *in-situ* measurements on thin films in order to derive meaningful informations on size effect.

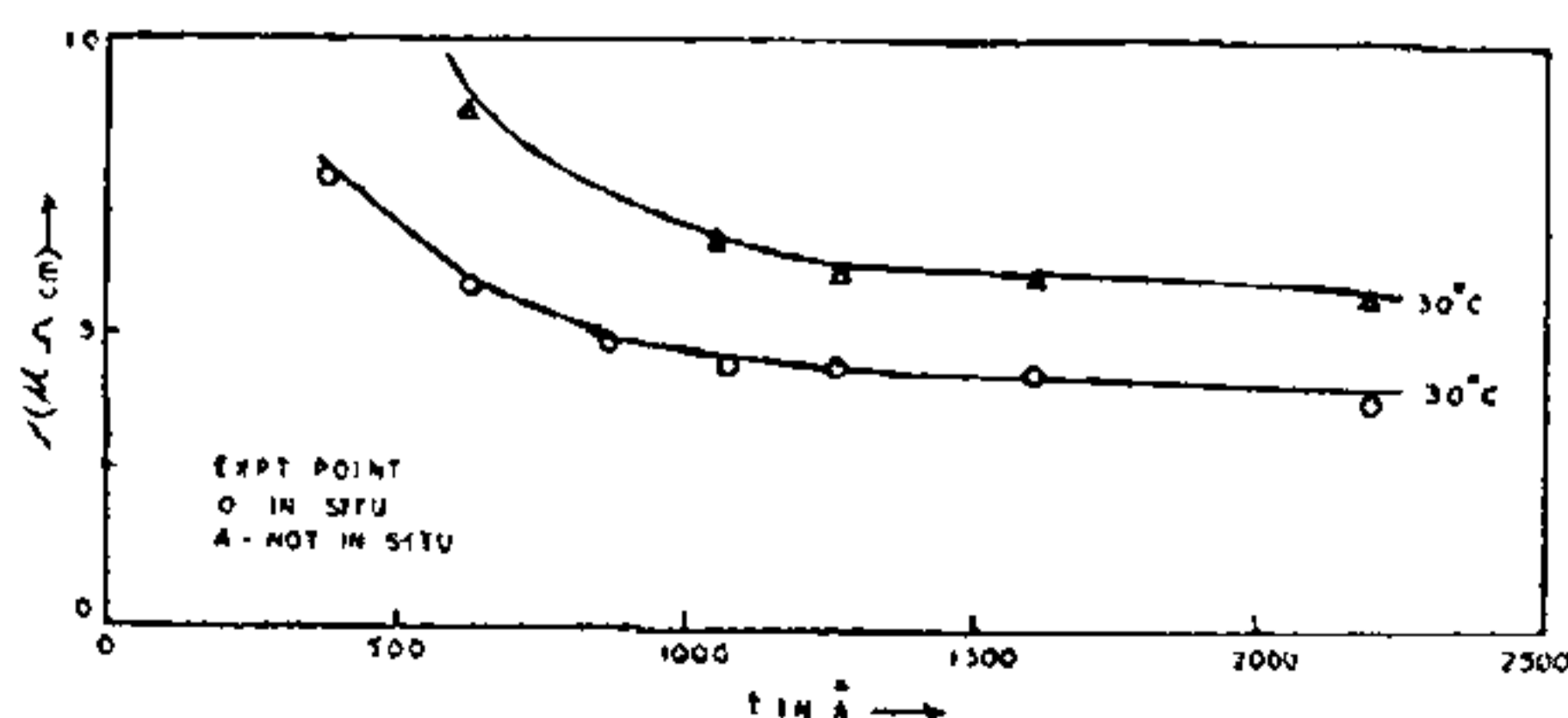


FIG. 1. Resistivity ( $\rho$ ) of silver films as a function of thickness ( $t$ ) at room temperature.

\* This is a part of the Ph.D. work of the author.



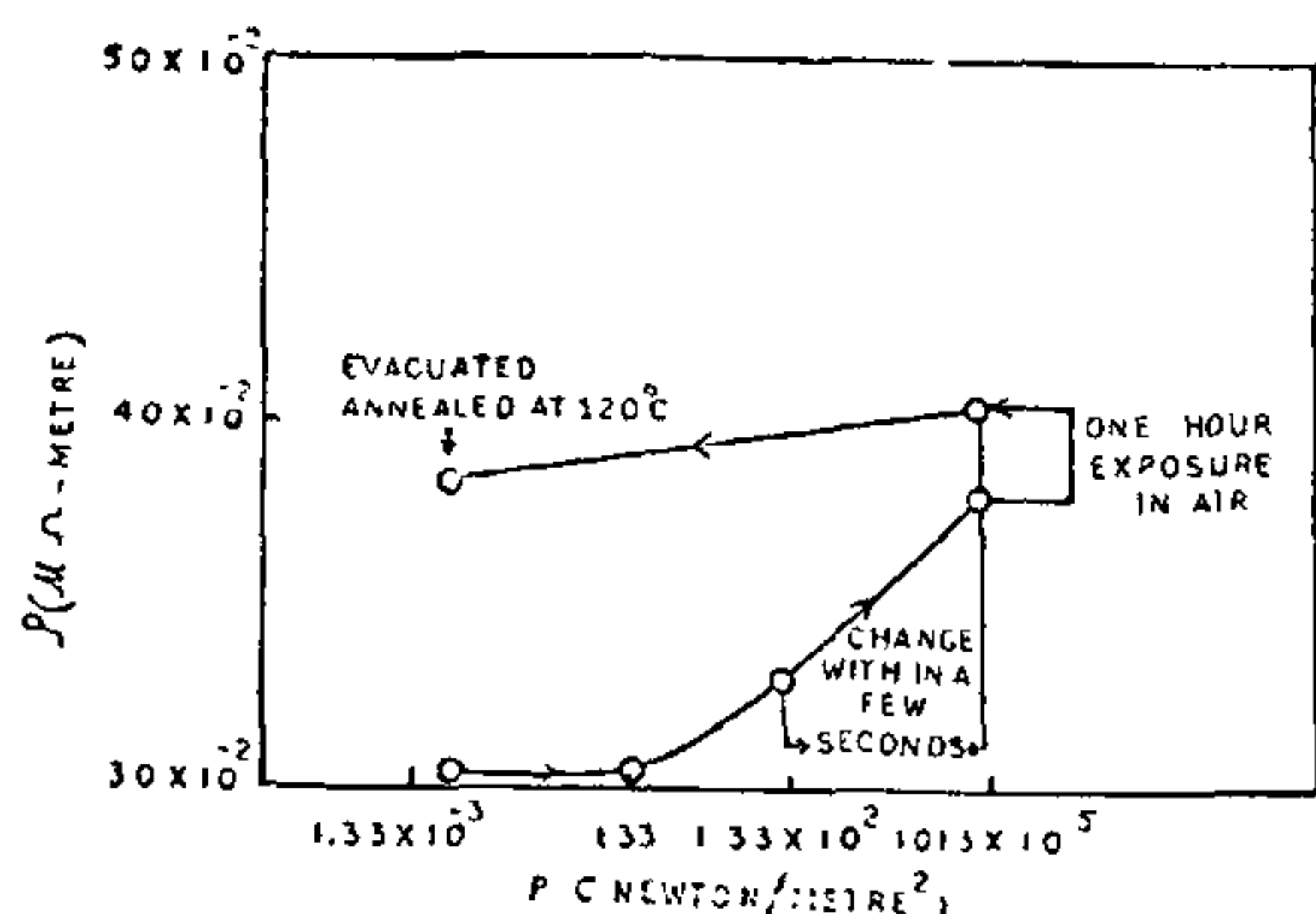


FIG. 2. The dependence of the resistivity ( $\rho$ ) of a copper film (thickness = 300 Å) on the residual atmosphere at room temperature (30°C).

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### DIRECT SPECTROPHOTOMETRIC ESTIMATION OF CADMIUM

THE literature survey reveals that there is hardly any direct spectrophotometric methods of analysis of cadmium. The present communication reports the direct spectrophotometric estimation of cadmium with 5, 6-dibromo, 2, 3, 4-trihydroxyacetophenone (DBTHAP). The method is very simple and gives satisfactory quantitative results.

The bluish green coloured complex has a maximum absorbance at 590 nm in the pH range 9-10. The colour of the complex is stable for 20 minutes. Beer's law was varied between 20 and 90 p.p.m. of Cd(II).

The molar composition of the complex as obtained from Job's method of continuous variation was found to be 1:1. The molar extinction coefficient was found to be  $1.1625 \times 10^3$ . Sandell's sensitivity is  $0.1 \mu\text{g}/\text{cm}^2$  for  $\log I_0/I = 0.001$ . The optimum concentration range for the effective determination of Cd(II), evaluated from Ringbom's plot was found to be 36 p.p.m. to 54 p.p.m.

The polarographic study of the cadmium—DBTHAP complex shows a transient existence of  $\text{Cd}_2^{2+}$ . The fact that the complex is not very stable probably explains  $\text{Cd}_2^{2+}$ —DBTHAP complexation, which dissociates and cadmium is hydrolysed after some interval of time.

### Interference Due to Other Ions

The effect of diverse ions was studied by adding to  $\text{Cd}^{2+}$  solution various ions ten times in excess. Ions like  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{B}_2^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ti}^{4+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^{2-}$ ,  $\text{MoO}_4^{2-}$  do not interfere. However, ions like  $\text{V}^{5+}$ ,  $\text{Tl}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{BiO}_3^-$ ,  $\text{S}_2\text{O}_3^{2-}$  interfere seriously and therefore should be absent. Cations like  $\text{Bi}^{3+}$  and  $\text{Pb}^{2+}$  precipitate under the experimental conditions.

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### KINETICS OF POLYMERIZATION INITIATED BY MANGANESE(III) ACETATE

MANGANESE(III) ACETATE has been employed as one-electron oxidant for organic substrates and the mechanism of oxidation is well established<sup>1</sup>. Some redox systems, manganese(III) acetate-substrate, have been used to study the kinetics of polymerization of vinyl monomers<sup>2</sup>. But there is no report in literature about the use of manganese(III) acetate alone as thermal and photochemical initiator of polymerization. For the first time the present study reports some aspects of manganese(III) acetate initiated polymerization of acrylamide.

Acrylamide (S.D's laboratory reagent) was recrystallised using chloroform. All the reagents used were A.R. in quality. Kinetic experiments were conducted in glass vessels (of capacity 80 ml) with an inlet and an outlet. The solutions of monomer, acid ( $\text{H}_2\text{SO}_4$ ) and sodium bisulphate were deaerated for about 45 minutes. Sodium bisulphate was added to maintain constant ionic strength. Manganese(III) acetate was added after the solutions attained bath temperature. The rate of disappearance of monomer was estimated by bromometry and the rate of disappearance of