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Synthesis, Characterization and CO_2 Gas Sensing of PANI Doped with MnO_2

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Abstract
Polyaniline (PANI) is a conducting polymer of considerable interest because of its chemical and environmental stability, optical properties and ability to exhibit a substantial increase in electrical conductivity on doping. In the present work, PANI was synthesized by chemical oxidation using aniline, hydrochloric acid and ferric chloride. Manganese dioxide (MnO_2) nanoparticles were prepared and incorporated into PANI at 5% and 10% by weight to obtain PANI–MnO_2 composites. Thick films were fabricated on chemically cleaned glass substrates by screen-printing using a binder consisting of 8 wt% butyl carbitol and 92 wt% ethyl cellulose. The prepared materials were characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and ultraviolet-visible (UV-Vis) spectroscopy. The XRD observations reported in the project indicate that pure PANI shows semi-crystalline behaviour, whereas the 5% and 10% MnO_2-doped PANI samples exhibit broad diffraction features consistent with an amorphous character. FTIR observations include the reported N–H stretching band near 2351.23 cm^{-1} and additional bands at 1517.98 and 1566.00 cm^{-1} attributed in the project to MnO_2. UV-Vis measurements show absorption features reported at 180 nm and 650 nm, with the composite described as optically stable in the visible range. Gas-sensing measurements were examined as a function of time, and the project data show a time-dependent sensitivity response for the doped material. The work demonstrates the feasibility of combining PANI with MnO_2 nanoparticles for the development of sensing films.
Keywords: *Polyaniline; MnO_2 nanoparticles; conducting polymer; nanocomposite; XRD; FTIR; UV-Vis; CO_2 gas sensing*

1. Introduction

Conducting polymers have attracted significant attention because they combine characteristics of conventional polymers with electrical and optical properties that are more commonly associated with inorganic materials. Polyaniline (PANI) is one of the most widely investigated conducting polymers because it is comparatively easy to prepare and possesses useful chemical stability, environmental stability and optical performance. An important feature of PANI is its doping behaviour. Modification of the polymer through suitable doping can produce a marked increase in conductivity, and this property has led to the description of conducting polymers as synthetic metals in the literature.

The electrical response of a conducting polymer can also be influenced by the incorporation of inorganic nanoparticles. In a composite system, the polymer provides a conducting and processable matrix while the nanoparticle phase can modify the structural, optical and sensing behaviour of the material. Manganese dioxide (MnO_2) is an inorganic material of interest for such composite formation. The present project therefore investigates PANI doped with MnO_2 nanoparticles at two concentrations, 5% and 10% by weight, with particular attention to structural, vibrational, optical and gas-sensing characteristics.

The main objective of the work was to synthesize PANI by chemical oxidation, prepare MnO_2 nanoparticles, form PANI–MnO_2 composites at selected weight percentages, cast the composite as a thick film and study the resulting material using XRD, FTIR and UV-Vis techniques. The gas-sensing response was then examined as a function of time. The experimental observations presented below are based on the values and graphs contained in the supplied project presentation.

2. Materials and Experimental Method

2.1 Synthesis of Polyaniline. For the preparation of PANI, 5 mL of aniline was taken in a beaker with 50 mL of distilled water and 2 mL of HCl solution. The mixture was stirred using a magnetic needle for one hour. In a second beaker, 6 mL of $FeCl_3$ was mixed with 50 mL of distilled water. This solution was added to the first solution with the help of a burette. A dark-green precipitate was obtained. The precipitate was filtered and dried for approximately 24 hours. The project identifies this process as chemical oxidation of aniline using $FeCl_3$.

2.2 Preparation of MnO_2 Nanoparticles. For the nanoparticle preparation described in the project, a 1 M NaOH solution was added to 50 mL of distilled water with continuous stirring. In

the next step, 2–3 g of AR-grade MnO_2 was added. The resulting mixture was stirred and then kept for settling overnight. The precipitate obtained was filtered and dried at room temperature. The resulting material was used as the MnO_2 nanoparticle phase for composite preparation.

2.3 Preparation of PANI–MnO_2 Composite. The composite was prepared by weight percentage. For the 5% composition, 1 g of PANI and 0.05 g of MnO_2 nanoparticle were crushed together in a homogenizer for approximately 10 minutes. The product obtained was identified as 5% MnO_2-doped PANI. For the 10% composition, the project records 1 g of PANI with 0.010 g of MnO_2 nanoparticle, followed by homogenization. These quantities are reproduced as stated in the supplied presentation.

2.4 Film Casting. Thick films were prepared using a screen-printing technique. The binder for screen printing was made by thoroughly mixing 8 wt% butyl carbitol with 92 wt% ethyl cellulose. PANI/composite powder was mixed into the binder to form a viscous paste. The prepared paste was screen printed onto a chemically cleaned glass substrate and dried at room temperature (303 K) for 24 hours. The resulting film served as the sensing material for subsequent characterization and gas-sensing measurements.

3. Characterization and Results

3.1 X-ray Diffraction (XRD). XRD was used to examine the structural characteristics of the prepared materials. The supplied project reports that pure PANI shows two diffraction peaks at $2\theta = 21.10°$ and 23.59°. These peaks are described as sharp and well defined, indicating a semi-crystalline nature of polyaniline.

For the prepared MnO_2 nanoparticle, the project reports diffraction peaks at 37.2°, 42.4°, 56.4° and 66.6°. These are attributed in the project to the (211), (301), (411) and (002) crystal planes, respectively. The presentation notes that MnO_2 may exhibit structures that can be related to chain, layered or sheet-like arrangements. The XRD pattern therefore provides evidence that the nanoparticle phase contributes a distinct structural signature to the composite system.

For the 5% MnO_2-doped PANI sample, the project reports a diffraction peak at $2\theta = 25.52°$ with FWHM = 4.02°. The presentation interprets this pattern as indicating an amorphous nature of the doped material. For the 10% MnO_2-doped PANI sample, the reported peak occurs at $2\theta = 25.34°$ with FWHM = 3.9°, and the corresponding graph is also interpreted as showing amorphous character. Thus, within the interpretation supplied in the project, incorporation of MnO_2 changes the diffraction appearance of PANI from the semi-crystalline pattern observed for pure PANI to broad features associated with an amorphous composite.

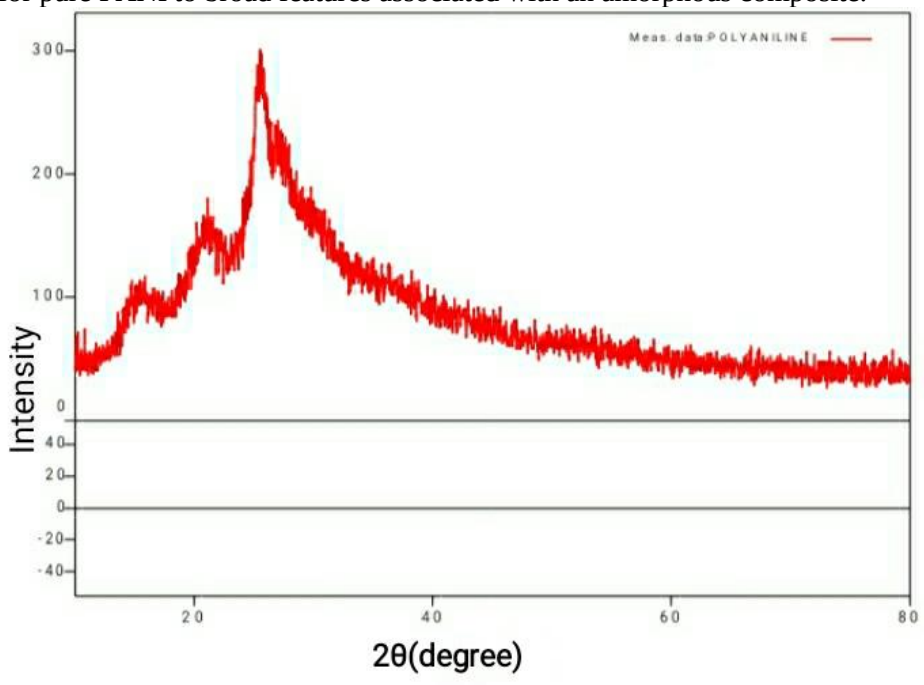


Figure 1. XRD pattern of pure PANI.

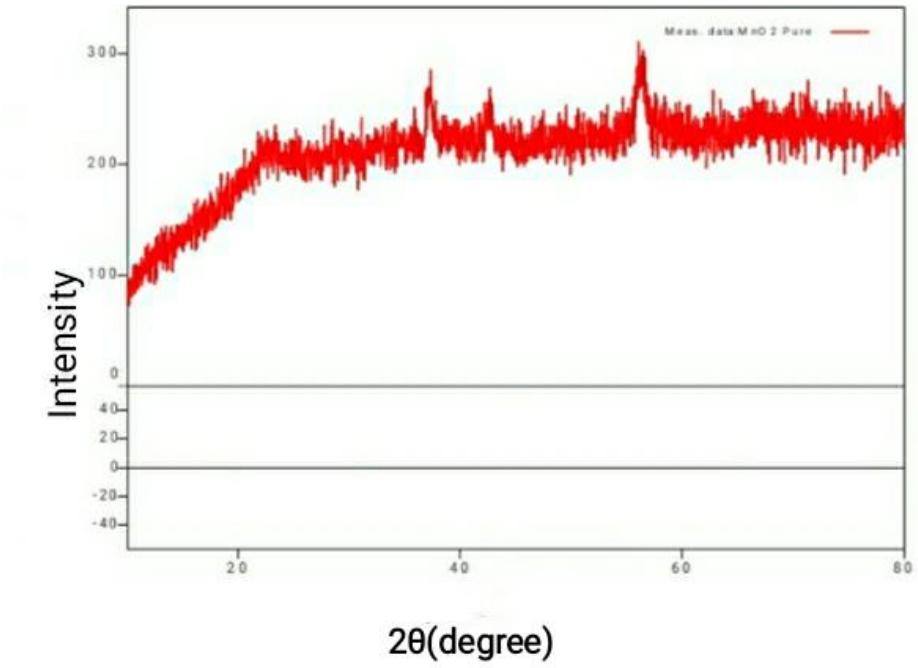


Figure 2. XRD pattern of MnO_2 nanoparticle.

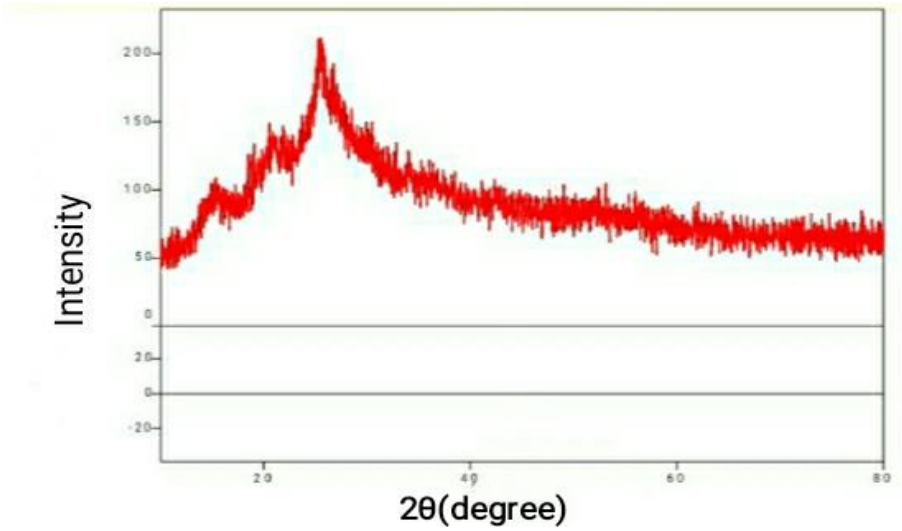


Figure 3. XRD pattern of 5% MnO_2-doped PANI

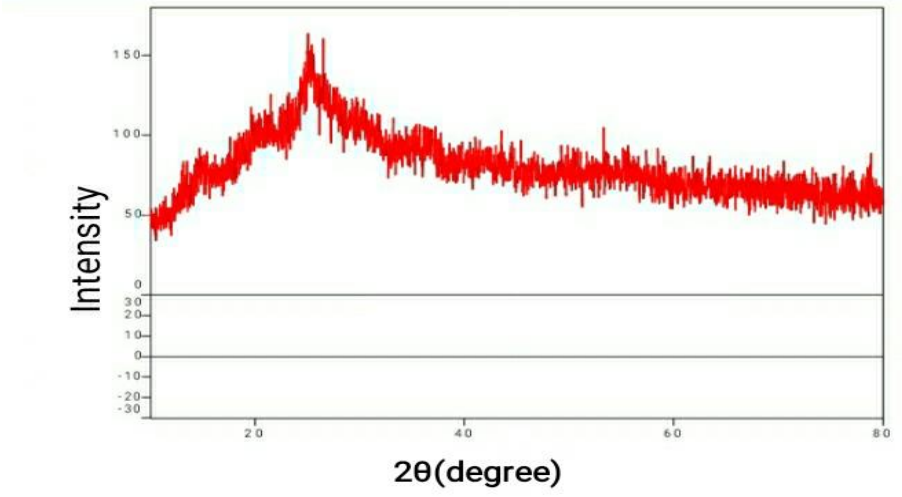


Figure 4. XRD pattern of 10% MnO_2-doped PANI.

4. FTIR Analysis

Fourier-transform infrared spectroscopy was used to examine characteristic vibrational bands of the prepared material. The project reports an N–H stretching band of an aromatic amine in the region of 2351.23 cm^{-1}. Additional bands reported at 1517.98 and 1566.00 cm^{-1} are attributed in the project to the MnO_2 nanoparticle contribution. The presence of these reported bands provides spectroscopic evidence for the chemical groups and components represented in the PANI–MnO_2 composite. FTIR therefore complements the structural information obtained from XRD by providing information based on molecular vibrations.

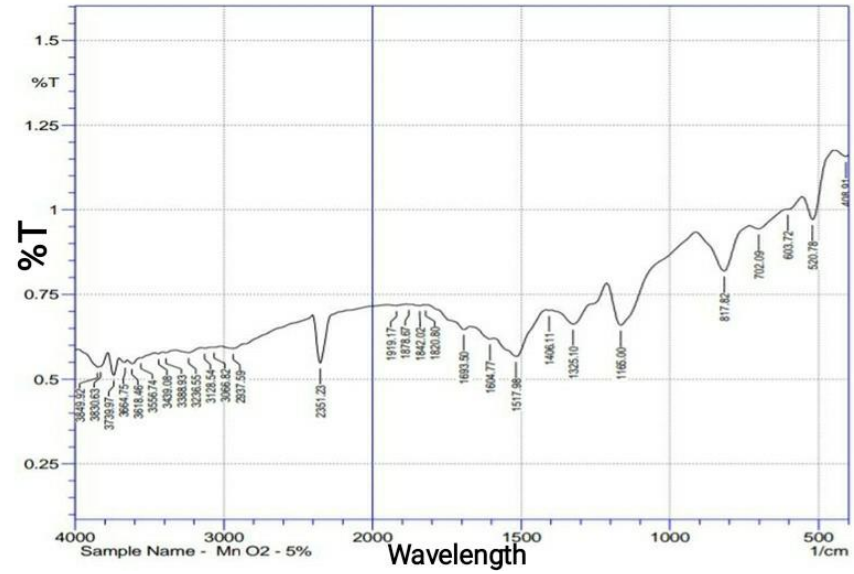


Figure 5. FTIR spectrum reported in the project

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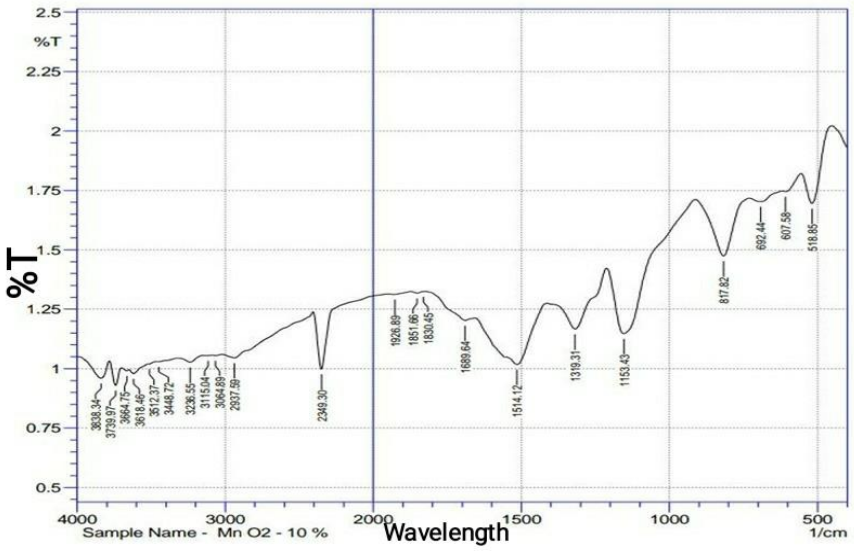


Figure 6. FTIR spectrum reported in the project.

5. UV-Visible Analysis

The optical behaviour of the PANI–MnO_2 nanocomposite was examined using UV-visible spectroscopy. The project presentation reports that the PANI–MnO_2 nanocomposite shows an absorption maximum at 180 nm and an absorption minimum at 650 nm. The material is described in the project as optically stable in the visible range and as potentially useful for optical-device applications where linearity in the visible region is required. The recorded UV-visible curves included in the supplied presentation show the absorption response as a function of wavelength and provide the optical characterization of the prepared composite.

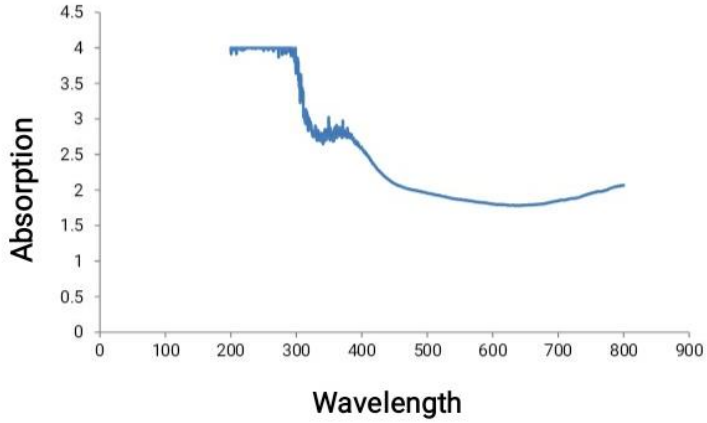


Figure 7. UV-visible absorption spectrum reported in the project.

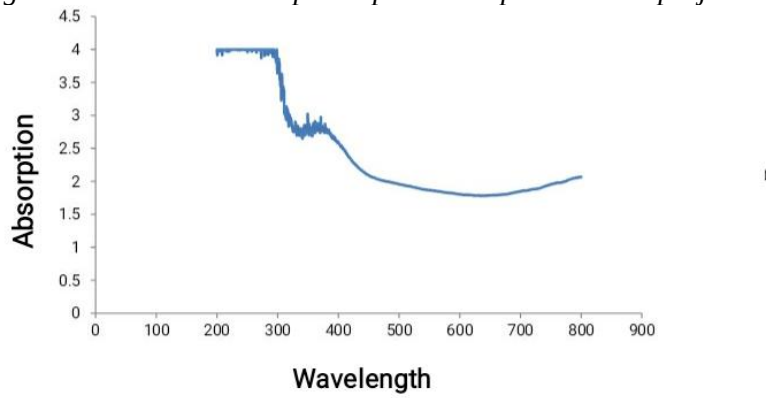


Figure 8. UV-visible absorption spectrum reported in the project.

6. Gas-Sensing Analysis

The sensing behaviour of the prepared material was studied as a function of time. The supplied project presents sensitivity-versus-time plots and associated numerical readings. The first data series recorded in the presentation gives sensitivity values of 0 at 0 s, 0.016187514 at 10 s, 0.016187514 at 20 s, 0.024373596 at 30 s, 0.032622168 at 40 s, 0.032622168 at 50 s, 0.032622168 at 60 s, 0.040933947 at 70 s, 0.049309662 at 80 s, 0.057750055 at 90 s, 0.057750055 at 100 s, 0.066255878 at 110 s and 0.074827894 at 120 s. This series shows an overall increase with time.

A second sensitivity series in the presentation records 0 at 0 s, 0.004723018 at 10 s, 0.007896039 at 20 s, 0.012694514 at 30 s, 0.014303995 at 40 s, 0.017538338 at 50 s, 0.020793347 at 60 s, 0.022428664 at 70 s, 0.024069222 at 80 s, 0.027366164 at 90 s, 0.030684376 at 100 s, 0.212795672 at 110 s and 0.174855819 at 120 s. The supplied project also contains a written observation stating that sensitivity increases with time and separately reports values of 0.0161 at 10 s and 0.989251 at 120 s, with a reported maximum of 0.312795 at 110 s and a minimum of 0.004723 at 10 s. Because these statements and plotted/tabulated readings are reproduced directly from the supplied project, they are retained here rather than silently altered or reconciled.

The project further reports that the sensitivity response is associated with changes in sample resistance. At the point identified in the written observation as the maximum, the sample resistance is reported as 7,851,635.53 Ω, while at the reported minimum the sample resistance is 947,766.2 Ω. Taken together, the gas-sensing measurements demonstrate a measurable time-dependent electrical response of the prepared sensing film. Such a response is the central functional outcome of the project and supports the investigation of PANI–MnO_2 as a material for gas-sensing applications.

7. Discussion

The results obtained from the different characterization techniques provide complementary information about the PANI–MnO_2 system. The XRD measurements distinguish the structural response of pure PANI from that of the MnO_2-containing samples. Pure PANI is reported as

semi-crystalline on the basis of its two comparatively sharp diffraction peaks, whereas the doped samples show broad features and are interpreted as amorphous. The shift and broadening of the diffraction response after incorporation of MnO_2 indicate that the structural arrangement of the polymer matrix is modified by the inorganic phase.

The FTIR observations further support the presence of characteristic chemical vibrations in the composite. The reported N–H stretching feature and additional bands assigned in the project to MnO_2 indicate that both the polymeric and inorganic components contribute to the spectroscopic response. The UV-visible measurements add an optical perspective, with the reported absorption features showing that the composite interacts strongly with electromagnetic radiation in the measured wavelength range.

The gas-sensing study is particularly important because it connects the material characterization with an application-oriented property. The time-dependent sensitivity response indicates that exposure and/or interaction conditions produce a measurable electrical change in the sensing film. PANI is suitable for sensing studies because its electrical properties can change when its conducting state is influenced by the surrounding environment. Incorporation of MnO_2 provides a composite interface that can further influence the electrical response. The present work therefore demonstrates a practical route from synthesis and film fabrication to functional sensing measurements.

8. Conclusion

Polyaniline was successfully synthesized by chemical oxidation using aniline, HCl and $FeCl_3$, producing the dark-green precipitate described in the project. MnO_2 nanoparticles were prepared and incorporated into PANI at 5% and 10% by weight as reported in the experimental procedure. Thick films were fabricated by screen printing on chemically cleaned glass substrates using the specified binder system.

The prepared materials were characterized by XRD, FTIR and UV-visible spectroscopy. Pure PANI showed reported diffraction peaks at 21.10° and 23.59°, corresponding to the semi-crystalline character described in the project. The MnO_2 nanoparticle showed peaks at 37.2°, 42.4°, 56.4° and 66.6°, while the 5% and 10% doped PANI samples showed broad peaks near 25.52° and 25.34°, respectively, and were interpreted as amorphous. FTIR and UV-visible measurements provided additional chemical and optical characterization. Finally, the gas-sensing study showed a time-dependent sensitivity response in the prepared material. Overall, the supplied experimental work demonstrates the feasibility of synthesizing PANI–MnO_2 composite films and investigating them for CO_2 gas-sensing applications.

9. Sensitivity Data Reproduced from the Project

The following numerical readings are reproduced from the supplied presentation without changing the reported values.

Time (s)	Sensitivity
0	0
10	0.016187514
20	0.016187514
30	0.024373596
40	0.032622168
50	0.032622168
60	0.032622168
70	0.040933947
80	0.049309662
90	0.057750055
100	0.057750055
110	0.066255878
120	0.074827894

Table 1. Sensitivity versus time data series reproduced from the supplied project.

Time (s)	Sensitivity
0	0
10	0.004723018
20	0.007896039
30	0.012694514
40	0.014303995
50	0.017538338
60	0.020793347
70	0.022428664
80	0.024069222
90	0.027366164
100	0.030684376
110	0.212795672
120	0.174855819

Table 2. Second sensitivity versus time data series reproduced from the supplied project.

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