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Final Report

Optimal Preparation of the ECC Ozonesonde

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Abstract

The ECC background current has been identfied as the removal of residual tri-iodide (iodine) as the cell approaches equilibrium. The altitude dependence of this source of the background current is expected to be only slowly changed in the troposphere with a more rapid decrease in the stratosphere. Oxygen does not play a role in the background current except in the unlikely situation where the electrodes have had all forms of iodine removed from them and the electrodes have not re-equilibrated with the sonde solutions before use.

A solution mass transport parameter in the ECC has been identified and its altitude dependence determined. The mass transport of tri-iodide dominates in the chemical transduction of ozone to electrical signal. The effect of the mass transport on the ECC background current is predicted.

An electrochemical model of the ECC has been developed to predict the response of the ECC to various ozone vertical profiles. The model corresponds very closely to the performance of the ECC in the laboratory. Based on this model, an ECC with no background current is predicted to give total ozone values within 1% of the correct value, although the vertical profile may be in error by as much as ±15%.

Introduction

This report presents the results of an evaluation of the tri-iodide/iodide electrochemical concentration cell (ECC) ozonesonde developed by Komhyr [1967, 1969]. The scope of the study was limited to the electrochemical and chemical reactions in the ECC to determine their effects on the reliability and accuracy of the sonde. Although the heterogeneous reduction of tri-iodide (iodine) at the cathode provides the measured signal in the sonde, a careful study previously had not been made of the factors in the sonde which affect the electrochemical reactions. A partial explanation of the previous observations of ECC responses, including those factors related to the pump, are presented here.

Torres and Bandy [1978] found that ECC sondes calibrated by an ultraviolet photometer have about a 10% variation (at the 90% confidence level) in ozone response. They also that the ECC total ozone values agreed with within 2% of the Dobson values but with a relative standard deviation of greater than 7%. Some of this variation may result from the background current correction. The observed background current varies from sonde to sonde. This is inconsistent with a simple oxygen-iodide reaction as the source of the background current. Variations in the way the air is sampled have been considered by Torres [1981], who has made a thorough study of the accuracy and reproducibility of the sampling pump efficiency.

The initial emphasis of this study was on the source of the non-ozone signal in the sonde and how it can be controlled, if not removed. Subsequently, a way was devised to evaluate the solution mass transport parameter in the sonde. This mass transfer parameter is the predominant term in the control of the ECC response to an ozone injection. Mass transport also plays a major role in the background current variation with time. The pressure-altitude dependence of the mass transport parameter was also determined.

The experimental results were then used to construct an electrochemical model of the ECC. An implementation of this model with a finite difference simulation of ozone injections closely matched the experimental performance of the ECC. Based on the electrochemical model, evaluations of the expected ECC responses to time-dependent ozone driving functions were made.

Summary of Results

The experimental procedures and the pertinent data are summarized in the attached articles by Thornton and Niazy [1982, 1983]. These articles also include detailed arguments concerning the source of the background current. A brief description of the salient points is given here along with a further exposition of the electrochemical model.

Background Current

The source of the background (non-ozone generated) current in the ECC has been identified as the reduction current arising from the removal of residual tri-iodide as the ECC approaches equilibrium. In the usual operation of the ECC, in which the electrodes have been in contact with the cell solutions for at least one day, there appears to be no response to oxygen. Consequently, the application of a pressure (altitude) dependent correction based on the decrease in oxygen with altitude has no justification on a cause-and-effect basis. Any altitude dependence in observed background current must have an explanation not related simply to the barometric equation.

Understanding that the background current occurs as a normal function of the cell as it approaches equilibrium, explains why in some circumstances the background current could be negative. The normal condition of preparation of the sonde's solutions is where the cathode solution has more tri-iodide than is allowed by the equilibrium condition imposed by the Nernst equation. Consequently, a positive background current of varying magnitude could be observed. The observation of a negative background current is simply the condition where the cathode solution has less tri-iodide than required to meet the equilibrium condition. The magnitude of the background current is variable since each sonde preparation could have differing amounts of initial tri-iodide. The background current appears time dependent because the removal (or generation) of the tri-iodide is dependent of the rate of the charge transfer reaction and the mass transport to the surface of the electrode where the charge transfer occurs. The electrochemical model described below provides a quantitative description of this relationship.

Because the background current arises from tri-iodide in excess of the equilibrium condition, it should be feasible to remove the excess so that before sonde flight there is no background current. There are several simple routes to this end. The simplest is to stir or shake the cell until the current goes to zero, or to some extremely low value, for example, 5 nA. Shorting the load resistor during this step will speed the process. Pumping air through the cell is not necessarily advisable because the solution will evaporate. Replenishing the solution is fruitless unless the solution has the same tri-iodide concentration as the solution to which it is added, that is, close to the desired equilibrium condition.

Alternatively, the tri-iodide could be reduced either electrochemically or chemically. Chemical reduction is simpler to implement because in involves only adding small quantities of a reducing agent until the background current reaches zero. However, a reagent must be used which will react rapidly and not interfere with the subsequent ozone measurement. Electrochemical reduction with a constant current source to a desired tri-iodide concentration avoids adding any other chemical species because the tri-iodide is reduced at the eletrode under the control of the externally supplied current. The disadvantage is the need to alter the cell connections to apply the external controls temporarily. Howvever, the solutions could be prepared separately using a constant current source to produce the desired tri-iodide concentration. The solutions could then added to the sonde.

Because the current observed in the absence of ozone is indistinguishible from the current when ozone is present, background current actually describes that current which exists as the cell approaches equilibrium before ozone sampling begins. When a source of ozone is connected to the cell and then is removed, the sonde current only slowly returns to the level before the ozone was injected. Approximately two minutes after the ozone was removed, the current may then appear as background current since no ozone input is occurring and a current exists. However, this is not true background current. It is a necessary condition of the operation of the ECC ozonesonde. Furthermore, it is theoretically not possible for the tri-iodide to return to exactly its initial level after the injection of ozone. This results from the production of tri-iodide in the anode half-cell, which establishes a new equilibrium condition. For small injections of ozone this new equilibrium condition is nearly the same as the initial condition. The cumulative effect of sampling ozone through the atmosphere produces in a final state quite different from the state at preflight.

Temperature also plays a role in the background current. When the temperatures of the half-cells are not the same, there will be a difference in potential between the half-cells, which will produce a current in the absence of ozone. The current persists until the new equilibrium is reached. As the temperature of the anode half-cell decreases, the solubility of the iodide decreases although the solution remains saturated in iodide. Consequently, the concentration of the anode tri-iodide does not remain constant, and the anode half-cell potential decreases. The net result would be to produce a positive current in the cell until the new equilibrium is reached. These effects are minor compared to the change in the background current that can occur as the mass transport parameter varies with temperature.

Mass Transport Parameter

The magnitude of the instantaneous current observed in the ECC ozonesonde is directly proportional to the rate of delivery of the tri-iodide to the electrode surface. While the rate of electrochemical reduction of tri-iodide is dependent on the magnitude of the shift from the equilibrium condition, the mass transport is essentially controlled by the rate of stirring in the cathode half-cell. This stirring in the cell is produced by the air bubbling through the cathode solution. Consequently, the mass transport rate constant will be dependent on the sonde's pumping rate.

The dependence of the mass transport paramter on pressure (altitude) is described in the attached paper [Thornton and Niazy, 1983]. The mass transport rate constant appears to be constant from 1000 mb to 100 mb. At pressures less than 100 mb, the mass transport rate constant decreases linearly with the logarithm of the pressure in mb. Of the two sondes tested, the mass transport rate constants for pressures of 1000 mb to 100 mb were not statistically different. Averages of the mass transport rate constants for the 16-19 mb range of the two sondes were different by about 9%. These differences can be ascribed to the differences in the pumping efficiency rates for the two sondes. The actual pumping efficiencies of these two pumps were not determined as described by Torres [1981].

The decrease in the mass transport rate constant with pressure can be explained in two parts. There will be a temperature dependent part related to the decrease in the diffusion coefficient of tri-iodide with temperature. The temperature dependence can be removed by dividing the mass transport rate constant by the diffusion coefficient at the corresponding solution temperature to obtain the diffusion layer thickness. At pressures less than 100 mb the diffusion layer thickness decreases with pressure. This decrease implies a decline in stirring rate because the diffusion layer thickness is inversely dependent on the solution velocity. The variation of the diffusion layer thickness parallels the average pumping efficiency curve [Torres, 1981].

The mass transport rate constant dependence with pressure implies that a background current observed at the ground should be nearly constant to pressures of about 100 mb. For pressures from 100 mb to 10 mb the background current would decrease approximately linearly with the logarithm of pressure. Although the driving force for small currents in the ECC is a small potential difference between the anode and cathode half-cells, the equilibrium potential of the ECC is such that the rate contant for reduction of tri-iodide is larger than the rate constant for mass transport. At very small potential shifts from equilibrium, the reduction current becomes linear with potential. As a consequence, the decrease in background current would be nearly linear with time as long as the mass transport is constant. In the laboratory, slow linear decrease in the background current with time is observed. The decrease in the background current with the logarithm of pressure reported by Komhyr probably occurred because the the balloon rise nearly at a linear rate with time.

Assuming that the background current would follow the mass transport rate constant dependence on pressure, there would be an overestimation of the integrated ozone values determined by ECC using the background current correction of Komhyr. For the pressure region 1000 mb to 100 mb the Komhyr correction would produce an error in total ozone of +1.2% per 0.1 uA of current for an integrated ozone value of 0.345 atm cm. For the region of 100 to 10 mb, the error would be +1.6% per 0.1 uA of current for an integrated ozone value of 0.345 atm cm.

Electrochemical Model of the ECC

An electrochemical model of the response of the ECC to an injection of ozone was developed using a modified Butler-Volmer equation [Bard and Faulkner, 1980]. The ECC current can be calculated for any shift in potential away from the the equilibrium cell potential. The basic assumption of the model is that the ozone-iodide reaction is fast and goes to completion with a one-to-one correspondence of ozone and tri-iodide/iodine. The variables and parameters which are included in the model are: temperature, ozone partial presssure, load resistance, cell resistance, charge transfer rate, mass transport rate, and solution volume. Various stages of the development of this model were presented at the Spring and Fall Meetings of the American Geophysical Union in 1982 [Thornton, 1982].

Digital simulations of the responses of the ECC model to injections of ozone have been carried out. Initial conditions typical of the actual use of the ECC are applied at the start of the model. As an additional initial condition, the so-called background current is set to zero. As discussed above, this is a reasonable condition although it is not the present practice in the field. The partial pressure of ozone injected into the cell is converted to an equivalent tri-iodide concentration. The potential difference generated by the change in tri-iodide concentration is calculated from the Nernst equation. This potential is then corrected for ohmic losses, and then is used as the input value for the modified Butler-Volmer equation. The mass transport rate constant is incorporated through the mass transport controlled current term in the Butler-Volmer equation. Similarly, the charge transfer rate constant is incorporated through the exchange current term using 4×10^{-4} cm/sec as the standard heterogeneous rate constant at 298 K.

The calculated current is then converted into equivalent ozone partial pressure, and the cathode and anode concentrations are altered in conjunction with the electrochemical reactions. The simulation then continues this core calculation for the next time interval for the desired ozone input. Usually a time interval of one second was used. This proved to be adequate since the 63% response time of the ECC to an ozone injection was 14 seconds or longer. For step changes in ozone the model provided an excellent match for the ECC measured signal under laboratory conditions (figure 1). A minor deviation is observed when the ozone is stepped to a lower value. The most significant difference is that the model returns to a steady state faster than the ECC.

The model was also used to predict the ECC response to a sawtooth ozone function (figure 2). As would be expected for a device with a 14 second 63% response time the ECC response is very dependent on the period and amplitude of the sawtooth. In all cases the peak ozone response was lower and shifted to later time than the input ozone function. When the input function was returned to and held at zero, the calculated response eventually returned to zero. This behavior is well known for step changes in ozone. Users of the ECC ozonesonde should be aware that the integrated ozone values from the ECC are more accurate than instantaneous ozone values.

Because the model appeared to yield responses very close to the measured ECC response, simulations of ozone vertical profiles were made. Ozone vertical profiles from ECC balloon flights published by the NASA Wallops Flight Facility Field Measurement Support Office were used as typical ozone vertical profiles. Because the ozone and pressure data were given at one minute interval, linear interpolations were made over each one minute interval to produce one second interval data. The ozone-pressure pairs were then input into the model, and the ozone partial pressures was calculated at each second.

When the calculated ozone partial pressures were compared to the input ozone partial pressures, the integrated ozone values from the model were 1% lower than the input integrated ozone value (figure 3). The errors in the instantaneous ozone partial pressures range from 0% to 15%. The cases where no error was found were almost always where the calculated response was changing from underestimating ozone to overestimating it. The minimal error regions appeared to be 1000 mb to 500 mb and past the ozone peak. The errors were usually less than 2%. These regions corresponded to very slow changes in ozone. Large errors in instantaneous ozone values were found wherever the ozone partial pressure changed rapidly with time.

Based on these studies the electrochemical model can provide a useful predictor of how the ECC ozonesonde functions, where improvements can be made and what are the likely responses would be, what are the estimated error limits are to variations in the ozone profile.

Conclusions

The ECC ozonesonde background can be eliminated by control of the preparation of the sonde solutions. In type 3A sondes the background current is predicted to decrease only slightly from 1000 mb to 100 mb and the decrease approximately linearly with the logarithm of pressure. The decrease in current at pressures less than 100 mb is affected by the sampling pump efficiency. Similar corrections for 1A, 2A, and 4A sondes could be estimated by the procedures developed for the 3A sonde.

An electrochemical model of the ECC ozonesonde indicated that total ozone measurements to balloon burst could be accurate to within 1%. Ozone vertical profiles could have errors as large as ±15%. Further improvements in ECC accuracy could be guided by this electrochemical model.

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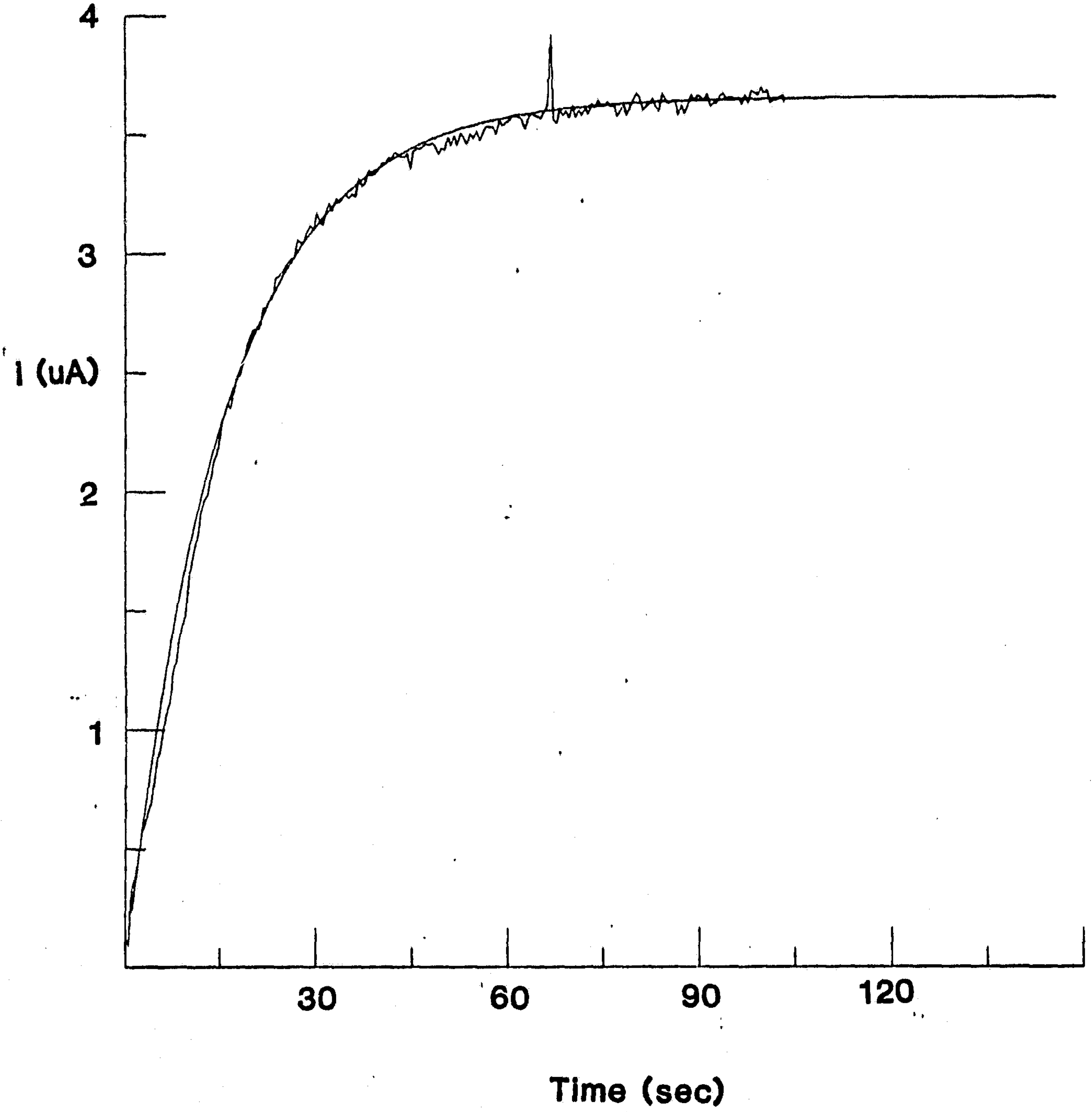

Figure 1A. ECC signal compared to electrochemical model for a step change in ozone to 128 nb from zero. Solid smooth line is model calculation.

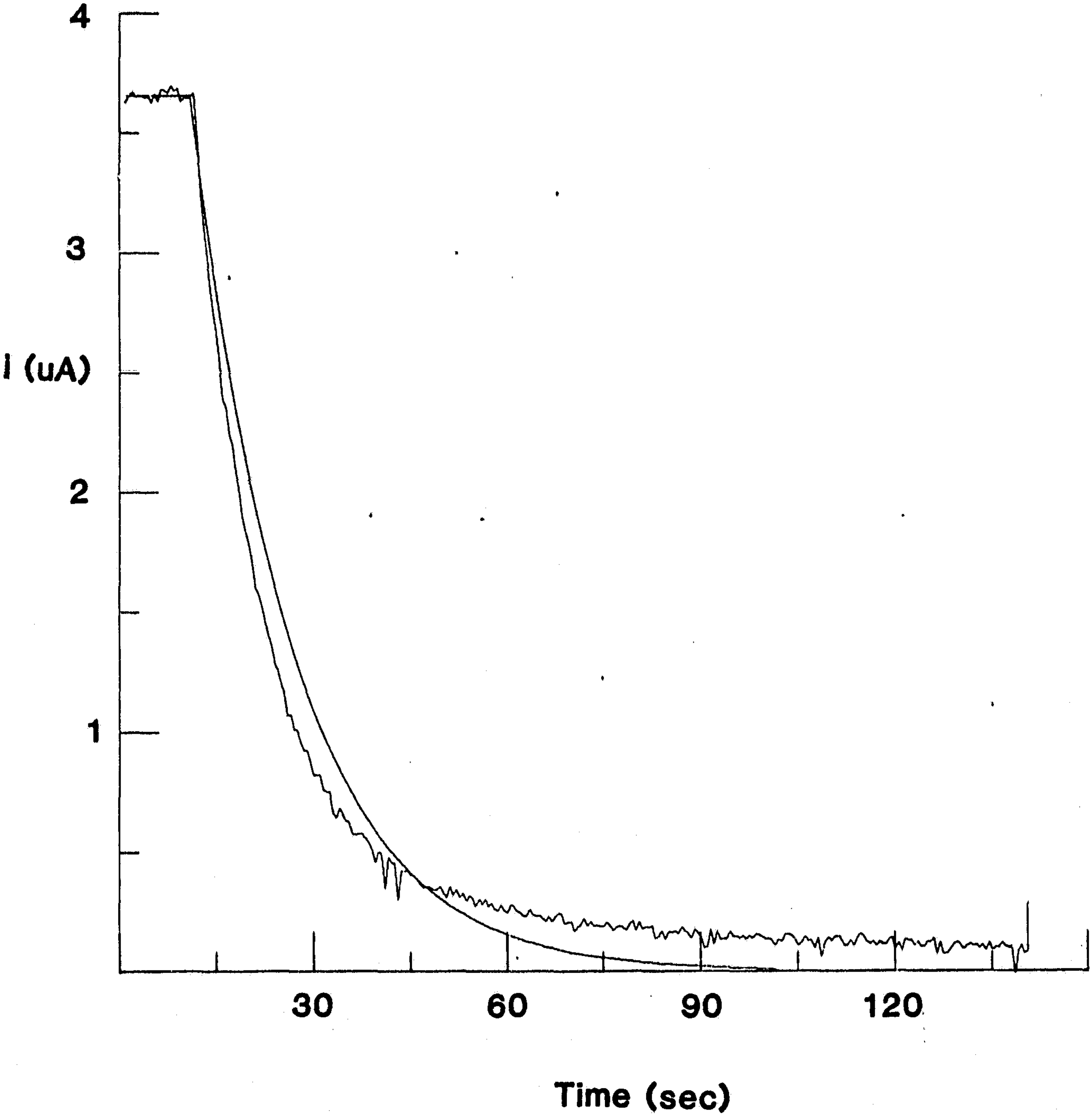

Figure 1B. ECC signal compared to electrochemical model for a step change in ozone to zero from 128 nb. Solid smooth line is model calculation.

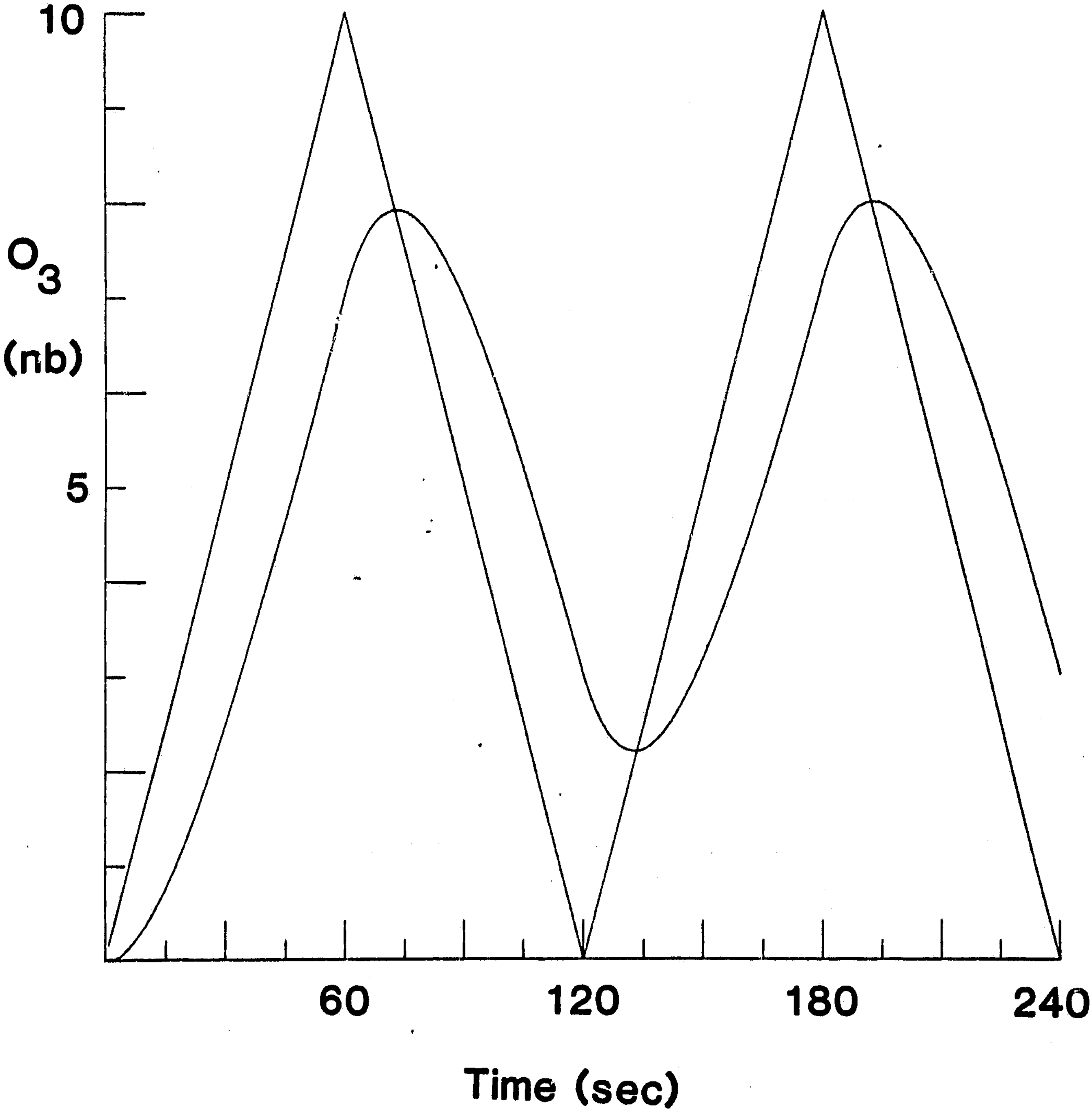

Figure 2. ECC electrochemical model predicted response for a sawtooth ozone input.

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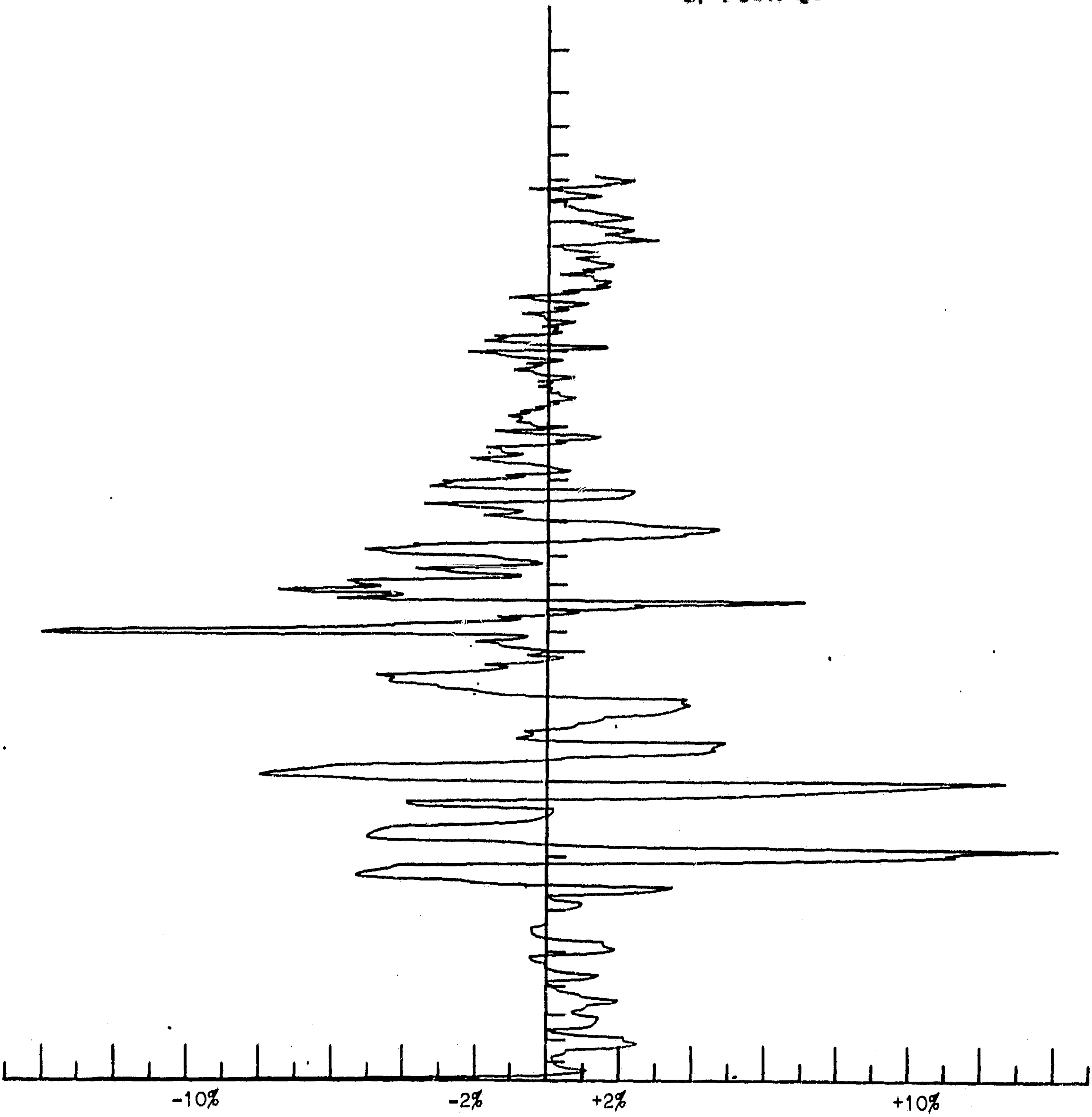

Figure 3. Relative errors in ozone partial pressure for digital simulation of ozone vertical profile.