the result may be of interest. The surface temperature was found to decrease by 0.11°K, from solar minimum to solar maximum, with flux changes described by the HT UV flux model. These results will be discussed elsewhere (L. B. Callis, M. Natarajan, J. E. Nealy, in preparation). Callis and Nealy (11) used a much simpler photochemical scheme (19 species, 41 reactions) than that used here and examined the effects of stepwise constant perturbations in the spectral solar UV flux of varying size rather than the continuous distributions shown in Fig. 1. Differences in results are attributed to a combination of these effects. Qualitatively, the results are the same.
14. Because of the difficulty in making the UV flux measurements and the lack of consistent coverage in time during the solar cycle, the error bars associated with the UV flux variability model postulated by Heath and Thekaekara (7) must necessarily be large. Therefore, two variations (see Fig. 1a) of the UV flux were used for the present analysis, that reported by Heath and Thekaekara and a modification of of this variation. The use of two flux perturbation distributions provides a comparison which illustrates the sensitivity of O_3 and temperature results (as a function of time and altitude) to such variations.
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Solar Constant: Constraints on Possible Variations Derived from Solar Diameter Measurements

Abstract. *Climatically significant variation of the solar constant (the energy output of the sun) implies measurable change in the solar radius. The available data limit variations of the solar radius between 1850 and 1937 to about 0.25 arc second; modeling of the sun indicates that the solar constant did not vary by more than 0.3 percent during that time.*

The sun is the predominant energy source for the terrestrial climate. It follows that an important step in an analysis of climatic change is a study of the changes, if any, in the sun's radiant energy output (the solar constant, S). Numerical models of the terrestrial climate indicate that the climate is, indeed, very sensitive to changes in S. However, reliable climatic simulations are difficult to construct because of the complicated feedback mechanisms involved in climatic change, and the present state of the art requires that the model predictions be treated with some caution (*1*). For this reason, historical data on possible variations in S, coupled with data on the climate for the corresponding periods, would be valuable in testing the climate models.

Direct measurements of S from within the atmosphere are difficult to make because of the large and variable absorption by the atmosphere. Two well-known studies have concluded that S has varied at about the 1 to 2 percent level within this century (*2, 3*), but these studies have been questioned because of the problems of atmospheric absorption and long-term calibration. Furthermore, variability at this level would indicate that the climate models are substantially in error since these models predict that such changes in S would cause climatic variations much greater than any that have, in fact, been observed (*4*). Space observations carried out in the last two decades have not detected significant variations in S (*5*). However, because of their limited accuracy (approximately 0.5 percent) and the short time span covered, these measurements cannot exclude the possible existence of long-term trends. Thus, long-term variations in S at the 1 to 2 percent level cannot be ruled out, and an independent check is highly desirable. Such an independent check can be provided by historical and recent measurements of the sun's diameter. We will show that historical diameter measurements constrain possible S variations to $\Delta S/S < 0.3$ percent for the period 1850 to 1937, and that current astrometric instrumentation could determine diameter changes corresponding to S variations as small as $\Delta S/S = 0.01$ percent.

In the outer layers of the sun, energy is transported from the interior to the surface by repeated emission and absorption of photons. The rate of this radiative diffusion of energy is governed by the temperature gradient. If S (and hence the diffusion rate) increases, the temperature gradient in the outer layers must also increase. This latter increase will be accompanied by other structural changes since the sun must maintain global hydrostatic equilibrium on time scales significantly longer than 1 hour (*6*). In general, a short-term increase in S will result in an increase in the solar radius, as will be discussed below. The magnitude of the change in radius corresponding to a given change in S must be determined by numerical solutions of the time-dependent equations of energy transport and hydrostatic equilibrium.

We define W as the ratio of fractional change in radius to fractional change in S

$$W = \frac{\Delta R/R}{\Delta S/S}$$

The value of W will, in general, depend on the nature of the change in the sun's structure that gives rise to a change in S; so, ideally, the physical mechanism responsible for the change should be specified and explicitly modeled. In practice, this is not possible since the mechanism is not known. Instead, we adopt the procedure of specifying (on physical grounds) the depth in the sun at which the perturbation arises and the time scale on which it occurs. We emphasize that these two parameters are not independent and, furthermore, that the time scale is constrained by the time period over which changes in S (or lack thereof) are observed.

The changes in S implied by the studies of (*2, 3*) apparently occur over periods shorter than 10^2 years and we adopt this as the relevant time scale. This immediately rules out any possible changes in the core of the sun since such changes require approximately 10^6 years (the photon diffusion time) to propagate to the surface and the change in S would be spread out over a similar time scale. This forces us to look closer to the surface.

The outer layers of the sun are unstable to convective motions, with the convective region extending from the surface to about 12 percent of the distance to the center. The thermal time scales (*6*) in the convective region range from about 2×10^4 years at the bottom to essentially zero near the surface. Over most of this region, convection is very efficient and carries essentially 100 percent of the thermal flux. Since the temperature gradient is nearly adiabatic (and will remain so for any reasonable changes in the convective flows), it is difficult to imagine a perturbation in this region that would lead to a substantial change in S. Near the surface (at a depth of less than 1 percent of a solar radius), the convection becomes less efficient because of the decreasing density, and radiative transport becomes increasingly important. A change in the efficiency of convection here would change the flux of energy carried by radiative diffusion, and

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hence the physical structure of the affected regions. Such a perturbation would be most effective near the transition zone, where convection still carries a significant portion of the total flux. For example, if the convective flows were perturbed in such a way that the efficiency of convection increased, this would release additional energy into the upper layers. There, the energy would have to be carried by radiative diffusion. This would lead to an increase in the temperature gradient and radius, accompanying an increase in S.

The change in the convective efficiency could be due to a change in the magnetic field configuration or to the inherent instability of the turbulent flows that characterize the convection zone (*7*). The former change might occur in some fraction of the 22-year solar magnetic cycle, while the latter change would be characterized by a (much shorter) dynamical time scale. In either case (and for any other short-term perturbation), the resulting change in S and radius would propagate to the surface on a thermal time scale ($\lesssim 10^2$ years). To simulate this effect, we have computed solar models in hydrostatic (but not thermal) equilibrium while varying the efficiency of the convection within a time series of models, using a standard (Henyey) time-dependent stellar evolution code. The procedure is similar to that of Dearborn and Newman (*8*), except that we introduce changes on much shorter time scales. From the models, we find that for changes in the convective efficiency occurring on time scales shorter than 10^3 years

$$W \simeq 0.075$$

Thus, a 1 percent change in S should lead to a 0.075 percent (or 0.72 arc second) change in the solar radius. We emphasize that we have not explored in detail how this result depends on the form of the perturbation, although we do not expect other forms (for instance, a depth-dependent change in the efficiency of convection) to produce radically different results. As an estimate of the model dependence of this result, we note that W is observed to be approximately 0.1 for a wide variety of radially pulsating stars (*9*). Since both the source and time scale of the variability in such stars are very different from those of our simulations, it appears that W is determined more by the energy transport equations than by the details of the perturbations.

Given a reasonable ephemeris for the earth-sun distance, the solar radius can be determined by measuring the angle subtended by the sun in the sky. Until recently, such measurements were routinely carried out at major national observatories as a by-product of observations of the right ascension and declination of the sun. Since there is no mark at the center of the sun's disk, the practice is to measure on the east and west limbs of the sun and to take the mean for the sun's right ascension. Then the difference gives the sun's horizontal diameter. Similarly, measurements on the north and south limbs, made to obtain the sun's declination, can be used to give the sun's vertical diameter.

Additional interest in such measurements was sparked by the suggestion, in 1872, by A. Secchi and P. Rosa of the Collegio Romano that the solar radius varies in phase with the 11-year sunspot cycles (*10*). Since 1872, several attempts have been made to confirm or disprove the so-called Secchi-Rosa law. Auwers (*11*) analyzed data from Washington, Greenwich, Neuchatel, and Oxford covering the period 1851 to 1883 and found no indications of periodic or continuous changes; he concluded that a variation as large as 0.2 arc second (where 0.1 arc second corresponds to 1×10^{-4} in $\Delta R/R$) correlated with the sunspot period was very improbable. For the period 1890 to 1903 Meyermann (*12*), using data from the Göttingen heliometer, found a fluctuation of 0.09 arc second, with no obvious correlation with the sunspot cycle. In contrast to these results, Cimino (*13*) found a variation of 0.6 arc second with a period of 22 years (the solar magnetic cycle period), based on measurements in Rome at Campidoglio Observatory from 1876 to 1938. The large amplitude of the variations found in Campidoglio data contradicts the earlier results, which should have been sensitive to such variations. In an effort to confirm the Campidoglio results, Giannuzzi (*14*) studied Greenwich transit observations from 1850 to 1937. She also found a 22-year period, but with an amplitude of only 0.1 arc second. The measurements in the vertical direction are clearly freer of systematic effects than those in the horizontal. In the vertical direction, the maximum excursion from the mean is 0.6 arc second. The standard deviation is 0.20 arc second (compared to 0.27 arc second for the horizontal). There is evidence in both the horizontal and vertical directions for a slow systematic decrease of the observed radius by about 0.2 arc second over this time; although Giannuzzi removed this trend, we have not done so in forming the above standard deviations, nor have we used her biennial running mean. It seems probable that the data do not indicate variations in the radius greater than about 0.25 arc second over this period, in agreement with the results of Auwers and of Meyermann.

A limit of 0.25 arc second for variations in the apparent radius corresponds to $\Delta R/R < 2.5 \times 10^{-4}$. With the value of W derived from our simulations, this gives

$$\Delta S/S < 0.33 \text{ percent}$$

for the absolute value of the fractional change in S over the period 1850 to 1937. These results contradict both the 1 percent long-term trend claimed in (*2*) and, especially, the 2 percent solar-cycle modulation advocated in (*3*). Since apparent radius measurements are less affected by atmospheric conditions than direct measurements of S and do not involve major calibration problems, the results of (*2, 3*) appear to be incorrect. If we accept the results of Giannuzzi (*14*) on the 22-year periodicity in the solar radius, this would indicate a 0.15 percent modulation of S in phase with the solar magnetic cycle.

In light of the preliminary nature of our modeling, we cannot claim any great quantitative accuracy for our results. However, the results should be qualitatively correct, and they illustrate a powerful means for looking for historical (and future) variations in the frequency-integrated solar constant. These results can be extended and refined by further work in the following areas.

1) A detailed analysis of the dependence of W on the nature of the perturbation would give greater confidence in the quantitative estimates of ΔS.

2) Further analysis of historical measurements of the apparent solar radius could extend the results to earlier periods. Transit measurements date back to 1659, with reasonably accurate measurements dating from 1750 (*15*).

3) Measurements of the solar diameter with the SCLERA telescope (*16*) could provide a highly accurate monitor of future changes in S. The potential accuracy of such measurements is approximately 0.01 arc second, so this would give a factor of 20 improvement in sensitivity. Furthermore, comparison of such measurements with space observations of variations in S could provide an independent check on the value of W and aid in analysis of the historical data.

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Antibody-Selective Membrane Electrodes

Abstract. *Direct antibody-sensing membrane electrodes have been developed by immobilizing ion-carrier immunogen conjugates in a liquid membrane matrix. The resulting potentiometric probes measure specific antibodies with high selectivity over nonspecific antibodies in the physiological* pH *range. The electrode response is shown to arise from the selective interaction of the antibody with the membrane-bound immunogen.*

Efforts to develop potentiometric electrodes have not been successful in producing practical sensors for antibodies (*1*). We now describe new electrode probes in which conjugated ion carriers in a liquid membrane configuration are used to produce selective sensors for direct antibody measurements. The resulting electrodes achieve a reproducible response to the antibody to dinitrophenol (DNP) and to the antibody to bovine serum albumin (BSA), respectively, with a high degree of selectivity over other nonspecific antibodies in dilute serum samples.

The electrodes (Fig. 1) were prepared by incorporating membrane disks (4 mm in diameter and 0.2 mm thick) in commercially available (Orion Research 92 Series) electrode bodies. Membranes were formed by immobilizing the ion-carrier conjugates in polymer films. Polyvinyl chloride was chosen as the matrix for the DNP ion-carrier conjugate and triacetylcellulose was used to form the membrane for the BSA ion-carrier conjugate. The triacetylcellulose was chosen for the latter conjugate because of compatibility with the membrane constituents.

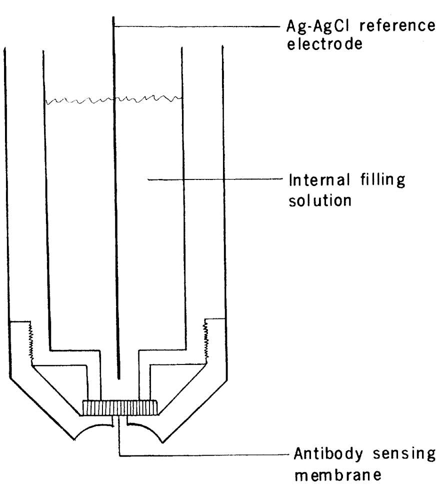
We chose dibenzo-18-crown-6 (*2*) as the ion carrier because its electrode properties have been well documented (*3*). The carrier was activated by nitration (*4*) and then reduced to the arylamine by tin (metal) and hydrochloric acid. The model hapten, DNP, was covalently coupled to the carrier by the Sanger reaction (*5*), whereas the BSA was coupled to the diazotized carrier.

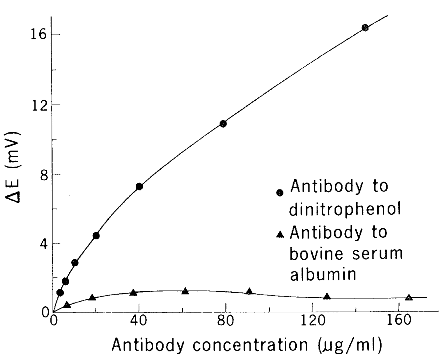
Potentiometric measurements at 30°C were compared to a single-junction reference electrode (Orion 90–01) in tris-HCl buffer (pH 7.5) and phosphate buffer (pH 7.2) for DNP and BSA, respectively. Because dibenzo-18-crown-6 is a cation carrier, all solutions were prepared to contain fixed amounts of either K^+ or Na^+, with the ionic strength adjusted to $0.154M$ with $CaCl_2$. This ensures that the observed potentiometric effects are the result of the immunochemical reactions and are not caused by changes in ion activities, pH, or ionic strength.

The results of potentiometric measurements carried out with the electrode for detecting antibody to DNP (anti-DNP electrode) are shown in Fig. 2. The electrode responds selectively to samples containing the antibody to the hapten conjugated to the ion carrier. The antibody to BSA is measured as a blank because the antiserum to DNP was produced by means of a DNP-BSA conjugate.

The potential response of the electrode for antibody to BSA is shown in Fig. 3. To prepare an appropriate blank sample, we treated the antiserum to BSA with immobilized BSA to remove the antibody to BSA (*6*). The electrode response to this "absorbed" antiserum shows a significant decrease in the magnitude of the potential changes.

As to selectivity, both the antiserum to DNP and the antiserum to BSA were in media of whole immune serums (Miles Laboratories) containing the full spectrum of serum proteins. Measurements were also carried out with membranes containing only the unconjugated ion





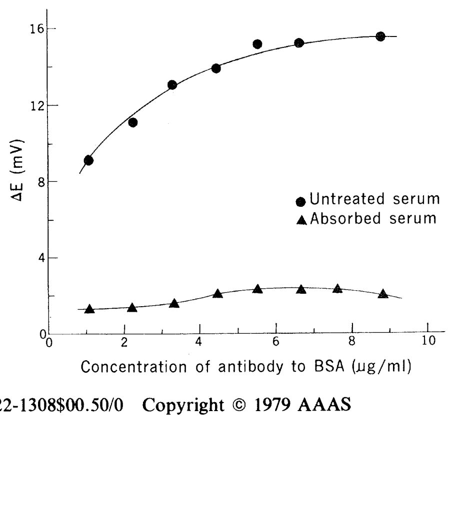


Fig. 1 (top left). Diagram of an antibody-sensing electrode. Fig. 2 (top right). Potentiometric response of the anti-DNP electrode to antibody to DNP and antibody to BSA in tris-HCl buffer (pH 7.5). ΔE is the change in potential relative to an Orion 90–01 single-junction reference electrode. Fig. 3 (bottom right). Potentiometric response of the anti-BSA electrode to antibody to BSA and the absorbed antiserum to BSA in phosphate buffer (pH 7.2). The untreated serum is whole antiserum to BSA and the absorbed serum is the immunoabsorbent-treated antiserum to BSA.