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ECC Ozonesonde Performance at High Altitudes: Pump Efficiency

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INTRODUCTION

The electrochemical concentration cell (ECC) ozonesonde was developed as a lightweight, balloon-borne instrument for measuring vertical profiles of atmospheric ozone (Komhyr, 1967; Komhyr, 1969; Komhyr and Harris, 1968). The sensor is based on a version of the familiar buffered-KI method wherein ozone oxidizes I^- to I_2. The atmospheric ozone concentration is calculated from a knowledge of the sampling-pump flowrate and the current flow during the electrochemical conversion of molecular iodine back to the ionic form.

ECC sampling-pump efficiencies decrease at high altitudes, necessitating the use of correction factors in ozone data at pressure-altitudes higher than about 50 hPa. A single correction-factor curve supplied by the manufacturer (Science Pump Corporation, Camden, NJ) is currently used for all ECC pumps. Essentially no information has been published concerning either the accuracy limits on this averaged curve, or how much variation is observed from one pump to another.

The work described below was undertaken to estimate the errors associated with using a single curve to represent the behavior of all ECC ozonesonde pumps. Apparatus was developed for high-precision measurements of the pumping-speed correction factors. Tests were conducted on a large number of standard model 3A ECC pumps, and on a smaller number of the newer model 4A pumps.

The correction factor considered here is defined by

$$C = S_0/S \tag{1}$$

where S is the pumping speed at some reduced pressure and S_0 is the high-pressure limit of S. Theoretical considerations suggest that the drop in pumping speed at low pressures is related to a combination of pump dead-volume and the hydrostatic back-pressure of the cathode solution against which the pump must work. These same considerations lead to a predicted dependence on ambient pressure (P_0), hydrostatic back-pressure (P_h), pump dead volume (V_d), and piston stroke-displacement volume (V_p) described by

$$C = (1 - P_h V_d / P_o V_p)^{-1} \tag{2}$$

Thus, C is unity (and $S = S_o$) if P_o is large or if P_h is small. Conversely, C is large at high altitudes where P_o becomes small.

The pumping speed can be determined by using the pump to pressurize a fixed-volume (V) container while measuring the time derivative of the pressure within the container (dP/dt). Assuming ideal-gas behavior, it can be shown that

$$S = \frac{V}{P_o} \frac{dP}{dt} , \tag{3}$$

where P_o is the pressure of the surroundings from which the pump draws air. For a given P_o, S can be determined from equation (3) if V is known and if dP/dt can be accurately measured at the appropriate point on the pressure-time curve.

If S is calculated from the initial slope when $P_h \approx 0$, then, from equation (2), C = 1 and $S = S_o$. If the slope is measured again when the container pressure equals $P_o + P_h$, then from equations (1) and (3),

$$C = \frac{S_o}{S} = \frac{(dP/dt)_{P_o}}{(dP/dt)_{P_o+P_h}} . \tag{4}$$

The correction factor C can thus be found from the slope ratio, and the container volume need not be known. Furthermore, the P_o value need not be measured with high accuracy. For small time intervals, Δt, equation (4) can be written as

$$C = \frac{(\Delta P/\Delta t)_{P_o}}{(\Delta P/\Delta t)_{P_o+P_h}} . \tag{5}$$

If the same pressure interval, ΔP, is used to determine both slopes, then equation (5) reduces to

$$C = \frac{(\Delta t)_{P_o+P_h}}{(\Delta t)_{P_o}} , \tag{6}$$

and the pressure interval itself need not be known.

The following section will describe apparatus which uses the same range of the same pressure transducer for the two ΔP measurements. Pressure transducer calibration errors and nonlinearities are thus both unimportant since their effects cancel in the ratio of equation (6).

EXPERIMENTAL

The apparatus used to determine the corrections is shown in Figure 1. Valves V1 - V4 are magnetically-latching valves switched by 40 ms pulses. The terms in equation (6) are determined using two small chambers, CH1 and CH2, and two electronic pressure transducers, DP (0.7 hPa full-scale) and DPH (7 hPa full-scale). The denominator of equation (6) is first determined by closing V2, V3, and V4, and measuring the time interval required to pressurize CH1 relative to CH2 by about 0.1 hPa. Valve V3 is then opened long enough for the ECC pump to pressurize <u>both</u> chambers up to the desired back pressure P_h (i.e., $P = P_o + P_h$) as indicated by the differential transducer labeled DPH. Valve V3 is then closed, and the time interval required to pressurize CH1 (relative to CH2) by the same 0.1 hPa increment is measured to give the numerator in equation (6).

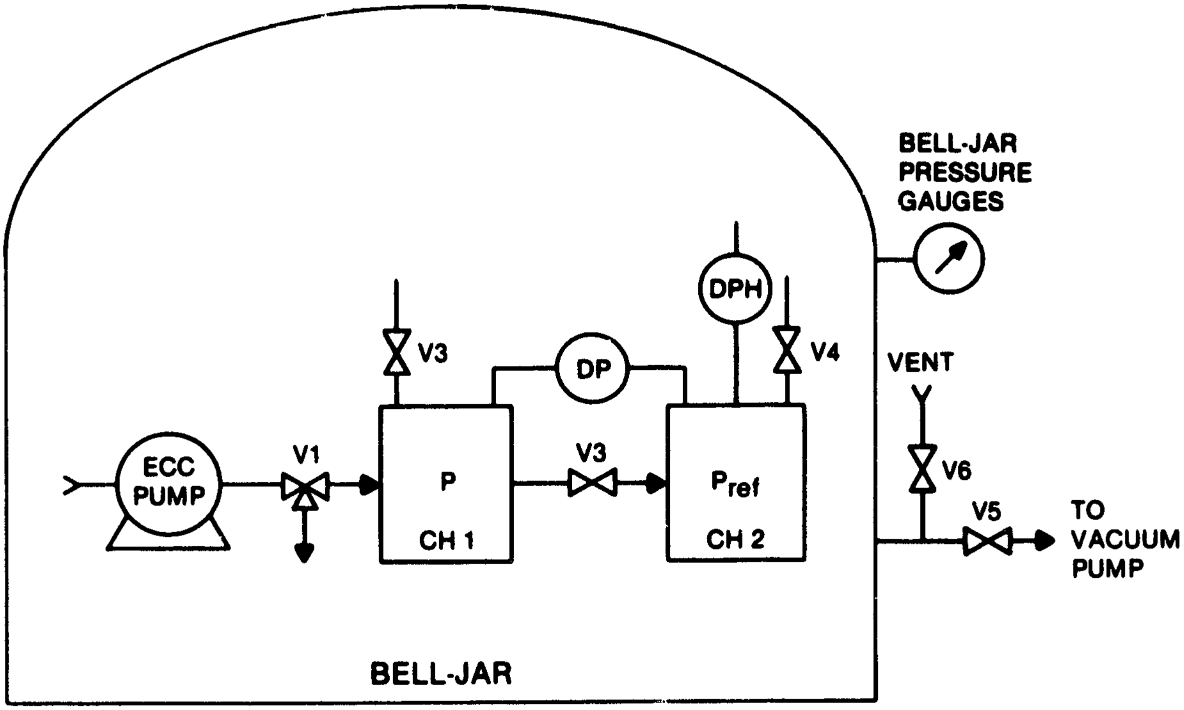

Figure 1. Apparatus used to measure pumping-efficiency correction factors. V1-V4 are magnetically-latching valves. DP and DPH are differential-pressure transducers.

The bell-jar is manually adjusted to the desired pressure using valve V5. This pressure is monitored by a combination of Heise (1067 hPa), Wallace and Tiernan (67 hPa), and Hasting (27 hPa, electronic) pressure gauges. Once the desired pressure is set, a microprocessor-controlled electronics package automatically sequences valves V1-V4 and does the timing.

The correction factor is sensitive to the cathode cell's hydrostatic pressure which varies as the solution evaporates during balloon ascent. An average P_h value was therefore determined at each atmospheric pressure for which the factor was to be measured. This was done by first examining data from a number of actual soundings to produce an average pressure versus time profile. Simulated soundings were then carried out in the bell-jar, measuring P_h while manually reducing the bell-jar pressure according to this pressure/time profile. The back-pressure was measured with an open-arm n-butyl phthalate manometer connected between the ECC pump and the cathode cell. The pressure levels and corresponding P_h values are listed in Table I.

TABLE I. HYDROSTATIC BACK-PRESSURES USED IN DETERMINING PUMPING-EFFICIENCY CORRECTIONS.

Pressure Altitude (hPa)	Hydrostatic Pressure (Pa)
60	269
40	261
25	254
15	234
11	216
8	204
6	194

RESULTS AND DISCUSSION

An indication of the measurement precision of the apparatus used in this study is given by the results listed in Table II. Pumping-speed correction factors for the same pump were measured six times during a period of about a week. The 1 S variation in the individual measurements at any pressure level averages about 0.5%. It should be noted that this small variation also reflects the stability of a particular pump's correction curve.

TABLE II. MEAN PUMP-EFFICIENCY CORRECTION FACTORS OBSERVED IN SIX TESTS OF THE SAME PUMP.

Pressure Altitude (hPa)	C ± 1 S
60	1.019 ± 0.009
40	1.032 ± 0.007
25	1.047 ± 0.005
15	1.078 ± 0.005
11	1.098 ± 0.004
8	1.129 ± 0.004
6	1.165 ± 0.004

A set of 43 model 3A ECC pumps were tested using this apparatus, with the results shown in Figure 2. The solid line shows the averaged correction factors with 1σ error bars. For comparison, the dashed line is the curve supplied by the manufacturer. Besides the bias of 2-3% from the manufacturer's curve, pump-to-pump variations become significant

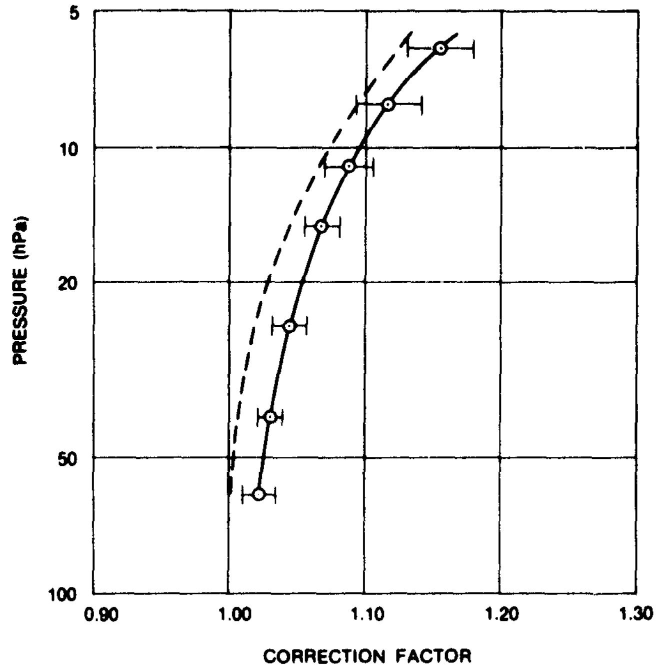

Figure 2. Mean pumping-speed correction curve found for a 43-sample set of 3A ECC pumps. Error bars represent one standard deviation. The dashed line is the manufacturer's curve.

at lower pressures. The 2σ value at 6 hPa, for example, is ± 5%. It should be noted that these pumps had consecutive serial numbers and were presumably from the same production batch. Variations from batch-to-batch would likely widen the error margin.

A seven-sample set of the new 4A-type ECC pumps was tested, and the results are shown in Figure 3. The averaged curve differs somewhat from that of the 3A versions, the correction factor being much closer to unity at high altitudes. Although the 4A error bars shown are about the same as those for the 3A pumps shown in Figure 3, their widths at pressures less than 11 hPa are reduced by about a factor of three if data for one particular pump is omitted from the set. Again, these pumps are probably from the same production batch.

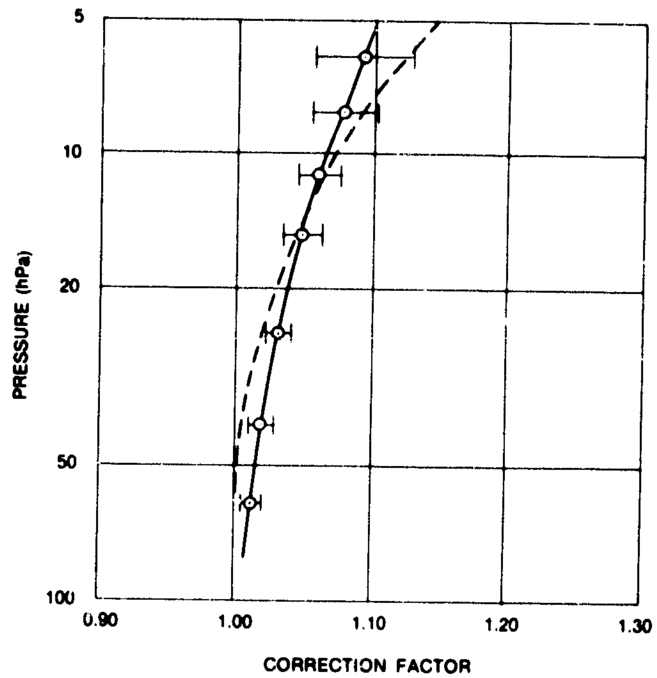

Figure 3. Mean pumping-speed correction curve for a seven-sample set of 4A ECC pumps. Error bars represent one standard deviation. Error-bar widths above 11 hPa are reduced by about a factor of three if only the "best six" are considered in the average.

The simulated hydrostatic pressures used in all of the measurements described above were electronically set and very reproducible. During a real sounding, variations in the evaporation rate will influence P_h, and this will have some effect on the correction factors (see equation (2)) at higher altitudes. At a simulated pressure-altitude of 6 hPa, for example, C was found to vary by about 0.09% Pa^{-1} when P_h was changed.

Another factor checked in this study was the effect of changes in the pump-spring tension. Tightening this spring reduces leakage under high back-pressure conditions, but can cause excessive current-drain on the motor battery. Although these spring-pressures are routinely checked and set to the manufacturer's specifications (about 10 kPa) during the preflight preparation, it was not clear how sensitive the pumping efficiencies would be to this adjustment at the hydrostatic pressures of the cathode solution. To determine this sensitivity, the pump-efficiency correction curve was measured for a pump at each of three different spring tensions covering a pump-pressure range (maximum pressure the pump will deliver) from 8.1 to 13.9 kPa. The results listed in Table III demonstrate that a wide range of pump-pressures is tolerable without significant effects on the correction factors.

TABLE III. PUMP-EFFICIENCY CORRECTION FACTORS AT DIFFERENT PUMP SPRING ADJUSTMENTS

	Pump-Spring Pressure (kPa)		
P (hPa)	8.1	11.9	13.9
60	1.016	1.028	1.022
40	1.034	1.042	1.030
25	1.054	1.500	1.470
15	1.076	1.077	1.073
11	1.102	1.096	1.096
8	1.143	1.132	1.133
6	1.178	1.170	1.162

CONCLUSIONS

Uncertainties of several percent in high-altitude ECC ozonesonde data result from variations in sampling-pump efficiency at reduced pressures. Differences among 3A-type ECC pumps are sufficiently large to justify individually calibrating each pump rather than using the averaged curve supplied by the manufacturer. The newer 4A-type ECC pumps offer the hope of improved performance, but a larger data set must be examined to demonstrate this conclusively.

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16. Abstract

ECC ozonesonde sampling pump behavior has been examined at pressures ranging from 60 to 6 hPa with the objective of evaluating uncertainties in high-altitude ozone data caused by variations in pumping efficiency. The averaged pump efficiency correction curve for a 43-sample set of 3A-type ECC pumps showed a 2-3% bias from the curve provided by the manufacturer. In addition, random pump-to-pump variations (2σ) were ± 5% at 6 hPa. These values probably represent minimum errors since the pumps were from the same production batch. A seven-sample set of the newer 4A type ECC pumps was examined, with similar findings as for the 3A types.

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