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Atmospheric Measurement Techniques
Discussions

An Automated Method for Preparing and Calibrating

Electrochemical Concentration Cell (ECC) Ozonesondes

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Abstract

In contrast to the legacy manual method used to prepare, condition, and calibrate the Electrochemical Concentration Cell (ECC) ozonesonde an automated digital calibration bench similar to one developed by MeteoSwiss at Payerne, Switzerland was established at NASA's Wallops Flight Facility and provides reference measurements of the same ozone partial pressure as measured by the ECC. The purpose of an automated system is to condition and calibrate ECC cells before launching on a balloon. Operation of the digital calibration bench is simple and real-time graphs and summaries are available to the operator; all information is archived. The parameters of interest include ozone partial pressure, airflow, temperature, background current, response, and time (real and elapsed). ECC cells, prepared with 1.0 percent solution of potassium iodide (KI) and full buffer, show increasing partial pressure values when compared to the reference as partial pressures increase. Differences of approximately 5-6 percent are noted at 200 nb. Additional tests with different concentrations revealed the Science Pump Corp (SPC) 6A ECC with 0.5 percent KI solution and one-half buffer agreed closer to the reference than the 1.0 percent cells, this is in agreement with results of multi-sonde comparisons obtained during BESOS. The information gained from the automated system allows a compilation of ECC cell characteristics, as well as calibrations. The digital calibration bench is recommended for ECC studies as it conserves resources.

1. Introduction

Measurement disagreement between similar or identical instruments seems to be an historical problem. Intercomparisons are generally conducted when new instruments are introduced and when operational changes or improved procedures become available. Such comparisons should be made under the same environmental conditions and include a reference instrument as an aid for checking the accuracy and reliability of the instruments. This would be ideal as a standard procedure. Unfortunately, balloon-borne ozone reference instruments are not usually available, mostly because they are too expensive for other than occasional use or to expend on non-recoverable balloon packages. Ozonesonde pre-flight calibrations are conducted, however these are basically single point calibrations made prior to its release. An automated system designed to condition and calibrate the Electrochemical Concentration Cell (ECC) ozonesonde was fabricated at Wallops Flight Facility. The automated system can provide calibration over a wide range of ozone partial pressures. This system, designated the digital calibration bench, enables consistent conditioning and calibration of the ECC along with measurements of a reference value. In this paper the term ECC refers only to the Science Pump Corp. (SPC) 6A ECC ozonesonde, although the automated system can accommodate the EnSci ozonesonde as well.

There are a variety of ground-, aircraft-, satellite-, rocket-, and balloon-borne instruments available to measure the vertical structure of atmospheric ozone and its total content. These instruments operate on different principles of measurement (Fishman et al, 2003; Kohmyr, 1969; Krueger, 1973; Holland et al, 1985; Hilsenrath et al, 1986; Sen et al, 1996). Although their spatial distribution is limited, balloon-borne Electrochemical Concentration Cell (ECC) ozonesondes have had a key role as a source of truth for the other instruments and for establishing algorithms necessary for the retrieval of satellite observations. Manual preparation of the ECC requires hands-on contact by an operator.

Reducing subjectivity is important and was considered serious enough to engage in the fabrication of the automated system. The user is prompted throughout the calibration process while utilizing real-time graphs and summaries. The digital calibration bench provides consistent preparation procedures. ECC measured ozone partial pressures vs. reference partial pressures are discussed and the results corroborated with similar comparison data obtained during the the 2004 comparison on the Balloon Experiment on Standards for Ozonesondes (BESOS) mission (Deshler et al, 2008) and with dual ECC comparisons at Wallops Island.

Notwithstanding efforts to enhance ECC performance (Smit et al, 2004, 2007, 2014; Kerr et al, 1994; Johnson et al, 2002; Torres, 1981) there remain uncertainties. Barnes (*1982*) and Barnes et al (*1985*) estimated the accuracy of the ECC as 5-10 percent and also pointed out that the accuracy varied with altitude. Uncertainties also arise from poor compensation for the loss of pump efficiency; erroneous background current; air flow temperature error and whether measured at the proper location; and, the use of the appropriate potassium iodide (KI) concentration. Understanding the influence these parameters have on the ozonesonde measurement capability is particularly important. The digital calibration bench is able to measure these parameters in a consistent way over a range of partial pressures.

2 Digital Calibration Bench Description and Operational Procedure

2.1 Description

The computer-controlled preparation and calibration bench fabricated at NASA Wallops Flight Facility follows the design of a similar bench developed by MeteoSwiss scientists B. A. Hoegger and G. Levrat at Payerne, Switzerland. The MeteoSwiss digital calibration bench was first available in the 1990's and continues to be used and is updated periodically. A comparable bench furnished by MeteoSwiss to the meteorological station at Nairobi, Kenya also has been in use for a number of years. The Wallops Island ozone site was interested in the digital bench because of its capability to provide precise and repeatable preparation of ECC's, and its automated feature requires less interaction with the ECC then the manual preparation method.

The Wallops digital calibration bench, shown in Fig. 1, consists of three major components: 1) mass flow meter to control air flow, 2) an ozone generator and analyzer (UV photometer), and 3) computer necessary to automate the timing of the programmed functions and process the data. Another important component, the glass manifold, enables the simultaneous distribution of the air flow to the ECC's and the UV photometer. The manifold also is a buffer maintaining constant air flow and inhibiting flow fluctuation. A graphical user interface controls the various input and output functions using an interface board and communications portal enabling synchronous communication protocols. A signal conditioning box allows connections to the ECC's analog signals that are conditioned with custom electronic components. Minor but necessary components include pressure and temperature sensors, and valves and solenoids to direct the flow of laboratory grade air. Calibration validity is accomplished by comparing the measured ECC ozone partial pressure against a reference partial pressure obtained with the UV photometer.

Fig. 2, from an unpublished technical note (Baldwin, private communication), illustrate the steps necessary to achieve a consistent calibration. By following the sequential flow diagram shown in Fig. 2, upper panel, the operator can better understand the sequence of tests. Each shape in the diagram is associated with a graphical window displayed on the monitor, as are notices that pop-up to instruct or direct the operator. The computer controlled digital bench follows the ECC preparation procedure in place at NASA Wallops Island at the time of the system's fabrication. Each ECC is recognized by its manufacturing date and serial number and includes the manufacturers test data. Changes to the steps are possible anytime through software reprogramming. Operationally, the preparation sequence begins by verifying whether ECC cells are new or were previously conditioned. A different path is followed for either condition. New cells are flushed with high ozone prior to manually adding KI solution. Cells previously having had solution added skip over the high ozone step to determine the first background current. Following the first background check the remaining steps are completed. Other measurements accumulated with the digital bench include motor voltage, motor current, pump temperature, and linear calibration at seven levels (0-300 nb). Program steps are displayed on the computer monitor with real-time information. All data are archived and backup files maintained.

Fig. 2, lower panel, illustrates the functional diagram detailing the essential operation of the digital calibration bench. Software control is shown in blue and air flow in green. Laboratory zero-grade dry air or desiccated compressed air is introduced into the ozone generator (TEI Generator) where a controlled amount of ozone is produced. The ozone flows simultaneously to the ECC cells and to the ozone analyzer (TEI Analyzer). The analyzer provides the reference partial pressure.

The measurement of the air flow and the corresponding time permits a precise flow rate to be determined. In contrast, the manual method uses a stop watch to estimate when 100 ml of air has flowed into a chamber. An experienced operator, using a volumetric bubble flow meter should be able to measure the time to within 1 second, possibly better. Although great care is exercised to obtain this measurement an error of one second is equivalent to an approximately three percent error in the measurement of ozone partial pressure. Further, the manual method requires that the effect of moisture from the bubble flow meter's soap solution be accounted for; flow rates determined with the digital calibration bench do not require a correction for moisture. Unfortunately, the calibration bench cannot determine the pump efficiency correction (PEC); this is taken into account differently. For a number of years, the ECC's PEC was physically measured at Wallops Island using a specially adapted pressure chamber (Torres, 1981). This system no longer is available. However, from its many years of use an extensive number of measurements are available. A sample of 200 pressure chamber measurements were averaged to obtain a unique PEC that was adopted for use at Wallops Island.

After eliminating deficiencies and improving functionality the automated system was tested while obtaining research data, primarily comparisons between different KI solution concentrations. Unfortunately, comparison with manually prepared ECC's was never contemplated. Calibration from 0 nb to 300 nb generally exceeds the nominal range of atmospheric ozone partial pressure. Calibration steps are made in 50 nb increments but larger or smaller increments are possible with minimal software reprogramming. Differences between ECC and reference measurements, if seriously large, provide an alarm to possibly reject the ECC, or after further study the differences between the ECC and reference calibration might be considered as a possible adjustment factor that would be applied to observational data.

2.2 Operational Procedure

ECC preparation procedures at Wallops Island are carried out five to seven days prior to preparing the ECC for flight. The pump, anode and cathode cells, and Teflon tubing are flushed with high amounts of ozone to passivate their surfaces and is followed by flushing with zero-grade dry air followed by filling of the cells. The cells are stored until ready to be used.

Operation of the automated system is simple, requiring only a few actions by the operator that include obtaining the first background current, air flow, 5 µA or high ozone (170 nb) test, response test, second background current, linear calibration between 0 nb and 300 nb, and the final background current. Two cells can be conditioned nearly simultaneously. i.e., the program alternates measurements between ECC's.

The operator must first determine whether the cell being conditioned had already been filled with KI or never was filled. Whatever the status of the cell (wet or dry) the operator must enter the identification information before proceeding. When a new, or a dry cell is to be processed the digital calibration bench initiates high ozone flushing. The program alerts the operator to turn on the high ozone lamp after which V3 of Fig. 2, lower panel, is switched to high ozone. The unit checks that ozone is flowing and after 30 minutes the program switches to zero air for 10 minutes and V3 switches back to the ozone generator. When completed, the operator is prompted by an instructional message on the monitor screen to fill the anode and cathode cells with the proper concentrations of potassium iodide (KI) solution. The cells are stored until ready for further conditioning and calibration before being used to make an observation. Considering that the ECC cell had been filled earlier with solution the digital bench instruction by-passes the high ozone flushing. Ozonesonde identification is entered, as above. The operator, after fresh KI has been added to the cell, is prompted on the monitor screen to begin the first background current measurement. In either case, whether a dry cell for which flushing is complete, or a wet cell ready for calibration, the procedure starts with clicking the OK button displayed on the monitor screen. After 10 minutes of dry air the background current is recorded. The background current record contains the following information: date, time in 1-2 second intervals, motor current, supplied voltage, pump temperature, and cell current. As the measurement is being made identical information is displayed graphically on the monitor. Following the background test all further steps are automatic.

Continuing to follow the steps outlined in Fig. 2, upper panel, the measurement of the air flow is accomplished on one ECC pump at a time by switching V1, shown in Fig. 2, lower panel, to the mass flow meter and at the same time V2 is switched to the glass manifold (ozone generator). When completed, V1 is switched back to the glass manifold and V2 is switched to the flow meter and the flow rate of the second cell is carried out. The air flow is output in sec/100 ml. The information stored includes: date, time in seconds at intervals of 7-8 seconds, mass flow meter temperature, atmospheric pressure, flow rate, and supply voltage.

Response of the ECC to ozone decay requires setting the ozone generator to produce 170 nb ozone partial pressure (approximately 5 uA). As ozone is produced the ozone level increases until the set level is reached. The elapsed time to reach this level is noted. The 170 nb of ozone is the reference level used to initiate the response test. After recording 170 nb of ozone for one minute the ECC response check begins. To measure the response, the cells would have to be switched to zero air quicker than the cell responds. This is accomplished by switching both cells (assuming two cells are being calibrated) to the mass flow meter, the source of zero air. This is more efficient than setting the generator to zero and waiting for the manifold and residual ozone in the system to reach the zero level. Thus, VI and V2 of Fig. 2, lower panel, are switched to the mass flow meter for immediate zero air and the program triggers a timer. The decreasing ozone is measured and recorded at five points used to reflect the cell response. As the ozone decays, measurements at 3-4 second intervals provide a detailed record of the response while also being displayed real-time on the monitor. The detailed record is hacked by the program at five points (1,

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2, 3, 5 and 10 minutes) successively and calculates the percentage of ozone change that occurred at the one-minute point which should be 80-90 percent lower than the reference of 170 nb. V1 and V2 are switched back to the ozone generator and the next 10-min background current measurement begins. The response record contains the following: date, time in seconds, motor current, supply voltage, temperature, mass flow, cell current, and atmospheric pressure. Data are displayed on the monitor in real-time.

The ECC cells have been conditioned and are ready for the linear calibration. The 0 nb to 300 nb calibration is performed. Step changes begin with 0 nb, followed by measurements at 50, 100, 150, 200, 250, and 300 nb. Each step requires approximately 2-3 minutes to complete allowing time for the cell to respond to each ozone step change. The linear calibration includes the reference measurement made simultaneously with the ECC measurement. After the upward calibration reaches the 300-nb level the calibration continues downward, to 0 nb. The measurements are displayed on the monitor for the operators use and also sent to an Excel file. Generally, the downward calibration experiences small differences from the upward calibration Only the upward calibrations are used.

Following the linear calibration, the final background current is obtained. As before this requires 10 minutes of zero grade dry air before making the measurement. The data are recorded.

A summary is provided of the calibration giving supply voltage, motor current, flow rate, pump temperature, response, and three background currents.

3 Digital Calibration Bench Practical Application

Repetitive comparison operations can be carried out with the digital calibration bench as often as necessary. This could result in a potential cost saving as there would not be a need to expend radiosondes, ECC's, and balloons. The testing with the digital calibration bench is limited to sea level conditions

3.1 Digital Calibration Bench (General)

Quasi-simultaneous testing of two ECC's is possible, enabling comparisons of different concentrations of KI solutions. Comparison of 2.0-, 1.5-, 1.0-, and 0.5- percent KI concentrations demonstrated that agreement with the reference improved with lower concentrations. Only the SPC 6A ECC's with 1.0 percent KI solution and full buffer (1.0%,1.0B) and 0.5 percent KI solution and one-half buffer (0.5%,0.5B) concentrations are discussed, however.

Testing indicated the pressure and vacuum measurements were nominal, some insignificant variation occurred but was not a cause of concern. Pump temperatures, controlled by the room air temperature, varied 0.1ºC to 0.2ºC. Motor currents showed some variation, some measured over 100 µA, suggesting a tight fit between the piston and cylinder. For example, one ECC motor current initially was 100 µA, a second measurement a week later the reading was 110 µA, a final reading after running the motor for a short time was 96.5 µA. Flow rates fell within the range of 27 to 31 seconds per 100 ml, a range comparable to flow rates manually measured with a bubble flow meter. Background currents were consistent. The lowest background current allowed by the digital bench is 0.0044 µA. The final background currents often were somewhat higher than background currents experienced with manual preparation, generally 0.04 µA on average. Final background currents obtained prior to a balloon release was in the range between 0.01 and 0.02 µA. Finally, the response of all the cells was good, falling within the necessary 80 percent decrease within less than one minute. Graphically checking a small sample of high-resolution responses found some variation as ozone decreased to 0 nb. The linear calibration (0-300 nb), is useful for comparing different KI concentrations.

3.2 Calibration and Potassium Iodide (KI) Solution Comparisons

As a practical example of the usefulness of the digital calibration bench is its capability to nearly simultaneously obtain measurements from two ECC's, one prepared with (1.0%,1.0B) and the second with (0.5%,0.5B). Conditioning of the ECC's followed the steps given in Fig. 2, upper and lower panels. In the free atmosphere ozone partial pressures usually range up to 150 nb to 200 nb. Linear calibrations to 300 nb are obtained, although a lower range may be reprogramed.

Figure 3 is a graphical example of differences between the reference ozone and the measurements of (1.0%,1.0B) and (0.5%,0.5B) KI concentrations. Rather than showing the differences from a single measurement, a sample of 18 digital bench measurements were averaged to give a more representative set of differences. Fig. 3 suggests that the two concentrations measured nearly identical amounts of ozone between 0 nb and 80 nb. Both curves begin to separate and diverge above 80 nb. The averaged data at 100 nb indicate that (1.0%,1.0B) is 3.6 nb, or 3.6 percent higher than the reference and (0.5%,0.5B) is 0.4 nb, or 0.4 percent higher; at 150 nb the difference is 6.7 nb, or 4.3 percent and 1.7 nb or 1.1 percent higher, respectively; at 200 nb the difference for (1.0%,1.0B) is 11.1 nb, or 5.5 percent and (0.5%,0.5B) is 4.8 nb or 2.4 percent higher, respectively. A check at the 300 nb level indicated (1.0%,1.0B) was 7.2 percent above the reference and (0.5%,0.5B) was 3.7 percent above. The ECC with (0.5%,0.5B) KI concentration is closer to the reference than (1.0%,1.0B) KI . Both ECCs' partial pressure curves have a slope greater than 1 trending toward higher amounts of ozone when compared to the reference value as ozone partial pressure increases. It is clear from the digital bench testing that the (1.0%,1.0B) KI solution increases at a faster rate than the (0.5%.0.5B) solution as ozone partial pressure increases. This non-linearity is not explained here. The intent of the examples is merely illustrative of the advantage provided by the digital bench to examine ECC behavior. Further, Fig. 3 indicates that the 1.0 percent KI measurement is further from the reference than the 0.5 percent KI while the percentage difference between the two concentrations is nearly constant at 3.2 percent, or in terms of a ratio between the two solutions, 0.968. Referring to the SPC ozonesondes compared during BESOS, Deshler et al (2017, Fig.5 and Table 2) indicates non-linearity between the (0.5%,0.5B) and (1.0%,1.0B) KI solutions and similar ratio values, 0.970/0.960 .

The digital calibration bench turned out to be an ideal tool to obtain repeated ECC calibrations. The digital bench can calibrate two ECC's nearly simultaneously reducing the need to expend costly dual-ECC balloons. A negative aspect, possibly, is calibration occurs under sea level conditions so cannot provide knowledge of ECC behavior under atmospheric conditions. A series of calibrations were performed over a period of three weeks. Two new ECC's were prepared with (1.0%,1.0B) and (0.5%,0.5B) KI solutions. Although a number of time-separated calibrations were conducted, only one three-week test is shown in Fig. 4a, b, c. The result shown is characteristic of similar calibrations performed over a similar number of weeks. The cells were flushed and fresh KI solutions were used with each weekly test. Calibration over the full range, 0-300 nb was carried out, only the 300 nb partial pressures are discussed. During the first week, Fig. 4a, the (1.0%,1.0B) KI solution was approximately 21 nb, or 7 percent higher than the corresponding reference value. The (0.5%,0.5B) KI solution was about 6-7 nb or about 2 percent lower than the reference value. A second calibration one week later, designated week two in Figure 4b, showed the ECC with the (1.0%,1.0B) KI solution had moved further away from the reference, about 27-28 nb or 9 percent higher (approximately 6-7 nb higher than during week one), while the ECC with the (0.5%,0.5B) KI was now 12 nb or 4 percent higher than the reference. A third calibration, week three in Fig. 4c, showed both ECC calibrations had moved again. The (1.0%,1.0B) KI calibration increased an additional 2 nb and was now about 30 nb, or 10 percent higher than the reference. The ECC with (0.5%,0.5B) KI increased an additional 1 nb and now was 13 nb, 4 percent higher than the reference value. Providing an explanation for the changes observed between week one and week three is difficult. Changes that might be due to improper preparation and conditioning procedures is not considered since, by definition, the digital bench is consistent in how ECC's are prepared, i.e., it is expected that carrying out the preparation would be repeatable from week-to-week. Consideration also must be given to the fact that the ECC has a memory. It is very possible that calibrations taking place following week one could still be under the influence of the previous measurement due to some impurity residuals present on the ion bridge. On the other hand, the changes could simply be a normal evolution of typical ECC performance.

The curves shown in Fig. 4a, b, and c merely show the calibrated ECC offset relative to a reference, or "true" partial pressure. To bring the ECC measurements into

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correspondence with the reference suggests that downward adjustment should be applied to each curve. However, how should such time-separated calibrations be treated; should only the final calibration (e.g., week 3) be used or an average of the three calibrations. Regardless, after obtaining a large sample of similar digital bench measurements it would be possible to design a table of adjustments relative to ozone partial pressure to be used to adjust in-flight ozonesonde measurements. However, the calibrations are made at sea level and cannot account for the influence of atmospheric pressure and temperature. Nevertheless, any adjustment seemingly would be in the right direction and would aid in obtaining more representative ozone values.

Although digital bench calibration comparisons are instructive, important comparisons have been made between ECC's and reference instruments using other methods. ECC measurement comparability have been quantified through in situ dual instrument comparisons (Kerr et al, 1995; Stubi et al, 2008; Witte et al, 2019), laboratory tests at the World Ozone Calibration facility at Jülich, Germany (Smit et al, 2004, 2007, 2014) and by occasional large balloon tests such as BOIC (Hilsenrath et al, 1986), STOIC (Kohmyr et al, 1995) and BESOS (Deshler et al, 2008). BESOS provided important performance information about the SPC 6A ECC and the EnSci ozonesondes. Only the SPC 6A ECC is discussed. However, these complicated large balloon experiments that seem to occur every 10 years are expensive. The environmental chamber used in the Jülich tests covers a full pressure range but is also expensive to use. The purpose here is to show a calibration method that is simpler to use and provides calibration that includes a useful reference value, and is complementary to other methods, such as employed in the Jülich Ozone Sonde Intercomparison Experiment (Smit et al, 2007).

BESOS was conducted from Laramie, Wyoming during April 2004, employed a large balloon carrying a gondola fitted with 12 dedicated ozonesondes. The gondola also carried an independent power supply, a multiplexer/transmitter, and a UV photometer. The photometer (Proffitt and McLaughlin, 1983) was used for over 20 years in various tests conducted at the Jülich facility. Other instruments included on the gondola are not germane to the present discussion. The ECC's were divided into two groups, each group consisting of six SPC-6A and six EnSci ECC's. Each group of six ECC's was further partitioned into two sub-groups. One sub-group was prepared with 1.0 percent fully buffered KI solution, the second sub-group was prepared with 0.5 percent KI and one-half the buffer. Only the two SDC-6A sub-groups and the UV photometer are of interest to this discussion. The BESOS test design allowed comparison of: the differences between (1.0%,1.0B) and (0.5%,0.5B) KI solutions; the differences between SPC-6A and EnSci ECC's; and, the differences between both ECC types and the reference photometer (Deshler et al, 2008).

The photometer data were noisy during the early portion of the flight and did not provide reliable data. The remainder of the flight experienced intermittent data loss, but overall sufficient data were available to carry out an analysis, particularly in the stratosphere (Deshler et al, 2008). Partial pressures lower than 60 nb are not discussed. The data were separated into two displays of ozone partial pressures as shown in Fig. 5a and Fig. 5b. The filled diamonds, filled triangles, and filled circles illustrate the ECC/photometer relationship.

The least-squares method was used to fit the ozonesonde data in Fig. 5a, b. The ECCs' with the 1.0 percent KI, shown in Fig. 5a, measured increasingly more ozone than the reference as the ozone partial pressure increases. There is 3 percent more ozone measured at 100 nb, and 5 percent more ozone measured at 150 nb, than the photometer reference. This is within reasonable agreement with the digital calibration bench estimates, of 3.6 and 4.3 percent, respectively. The relationship between SPC-6A ECCs' prepared with 0.5 percent KI solution and the UV photometer, shown in Fig. 5b, is in closer agreement with the UV photometer than the 1.0 percent KI solution. The 0.5 percent partial pressures are mostly the same as the photometer values, but a small negative slope can be discerned.

In the 1998-2002 period the Wallops ozone station released a number of dual-ECC balloons, twelve pair successfully provided measurements to 30 km, and higher. The ECC's were attached about 35 meters below the balloon and each ECC was separated 2 meters. Each pair was composed of an ECC with (1.0%,1.0B) and (0.5%,0.5B) KI solutions. The profiles were averaged, and are displayed in Fig. 6. The profiles are interesting in that the 1 percent ECC and the 0.5 percent ECC measured virtually the same ozone partial pressure until reaching 70-80 nb, at an atmospheric pressure of approximately 65 hPa. At this level the (0.5%,0.5B) ECC began to measure less ozone than the (1.0%,1.0B) ECC. A similar feature was noted in Fig. 3 where the separation of the ECC's with different concentrations occur at about 80-90 nb. Fig. 6 shows the maximum ozone level was about 140 nb, near 22 hPa, where (0.5%,0.5B) KI measured approximately 10 nb, or 7 percent less ozone than that of the (1.0%,1.0B) KI concentration. This difference is approximately 4 percent higher than the result given by the digital calibration bench results of Fig.3, where, at 150 nb, the difference between the ECC 1 percent KI and ECC 0.5 percent is 3.2 percent.

Given that the digital bench tests revealed the (0.5%,0.5B) KI solution is in closer agreement with the reference measurement than the (1.0%,1.0B) solution suggested that a KI solution with a weaker concentration may possibly give even closer agreement. A small number of dual ECC tests were carried out. The decision was made to try a solution of 0.3 percent with one-third buffer (03%,0.3B). Six sets of ECC's were prepared for calibration. Each dual ECC test consisted of one ECC prepared with (1.0%,1.0B) KI solution and one with (0.3%,0.3B) KI solution. The digital bench comparison result disclosed the (1.0%,1.0B) result replicated the earlier results discussed above. As assumed, the lower concentration was nearly equal to, or slightly less than the reference. Average values derived from the six tests are shown in Fig. 7. To corroborate the bench results three balloon-borne dual ECC sondes were flown, each with 1.0 and 0.3 percent KI solutions. Unhappily, the results were inconclusive: one flight showed (0.3%,0.3B) to be higher than (1.0%,1.0B), a second flight showed it to be lower, and the third flight showed (0.3%,0.3B) to be nearly the same value. Although the 0.3 percent solution might appear to be a better choice additional tests are necessary.

4 Summary

The concept of an automated method with which to pre-flight condition and calibrate ECC ozonesondes was originally considered by MeteoSwiss scientists over 20 years ago. Drawing on their expertise, a facility designated as the digital calibration bench was fabricated at NASA Wallops Flight Facility between 2005-2007. The digital bench was put to use immediately to study ECC performance, conduct comparisons of different KI concentrations, enabled ECC repeatability evaluation, as well as calibrating the ECC over a range of partial pressures, including associated reference values. Tests conducted with the digital bench were performed under identical environmental conditions. The digital bench eliminates the expense and time associated with making similar tests in the atmosphere.

Early use of the digital bench was to calibrate ECC's, prepared with (1.0%,1.0B) KI solution, over a range of partial pressures from 0 nb to 300 nb. Comparison between ECC's with (0.5%,0.5B) and (1.0%,1.0B) KI solution and comparing their measurements with simultaneously obtained reference values revealed both KI solution strengths were measuring more ozone than the reference. There was an increasing difference between the ECC's and the reference as the partial pressure increased. For example, the ECC measurements slope upward to increasingly larger differences from the reference ozone measurements, i.e., increasing from 4.3 percent higher partial pressure at 150 nb (Fig. 3) to about 7 percent higher at 300 nb.

An instruments ability to repeat the same measurement is important, however, ozonesondes are used only one time. (There are exceptions when an occasional instrument is found and returned, but, unfortunately because of Wallops Island's coastal location nearly all sonde instruments fall into the Atlantic Ocean rendering them unfit to be reclaimed). The digital bench provided the opportunity to obtain repeatable calibrations of the ECC. Results from testing ECC cells over a period of three weeks, one test each week, showed the calibration changed, e.g., about 10 percent for 1.0 percent KI and 4-5 percent for the 0.5 percent solution.

Results from the digital bench also corroborate differences found between SPC 6A ECC'c flown on BESOS and also with dual-instrument flights flown at Wallops Island. The difference between ozonesondes at a pressure of 22 hPa showed the (0.5%,0.5B) ECC to be about 10 nb lower than the (1.0%,1.0B) ECC.

The digital calibration bench provides a capability to apply a variety of test functions whereby the valuable information gathered helps to better understand the ECC instrument. Evaluating SPC ECC performance using an automated method diminishes the requirement for expensive comparison flights. The tests performed, i.e., KI solution differences, calibrations over a time period, and dual-instrumented balloon flights, were consistent, giving similar results. The tests described in this paper are simply examples of the digital bench utility. Furthermore, not mentioned earlier, the digital calibration bench preparation facility potentially could contribute to an understanding of separating ECC variability from atmospheric variability. Thus, the automated conditioning and calibration system provides valuable information, and as a useful tool should continue to be a valuable aid.

5 Data Availability

Data are available from the authors.

6 Author Contribution

The first author acquired and prepared the data for processing and the second author was instrumental in certifying the digital calibration bench was working properly. Both contributed equally to manuscript preparation.

7 Competing Interests

The authors declare they have no conflict of interest.

8 Disclaimer

None

9 Acknowledgments

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11 Figures

Fig01. Digital calibration bench showing operational configuration and mounting position of two ECC ozonesondes. The major instrumentation includes ozone generator and analyzer, computer, flow meter, and glass manifold.

Fig02. Digital calibration bench diagrams showing a) sequential steps, and b) functional steps.

Fig03. Simultaneous measurements of ECC ozonesondes, prepared with different KI solution concentrations. Average differences are shown between 1.0 and 0.5 percent KI strengths. The blue curve represents (1.0%,1.0B) KI, the red curve (0.5%,0.5B) KI and the reference curve is shown in black. Calibrations are made in 50 nb steps from 0 nb to 300 nb.

Fig04. Calibrations of two ECC ozonesondes, one using 1.0 percent KI solution and the other 0.5 percent KI, over a three week period.

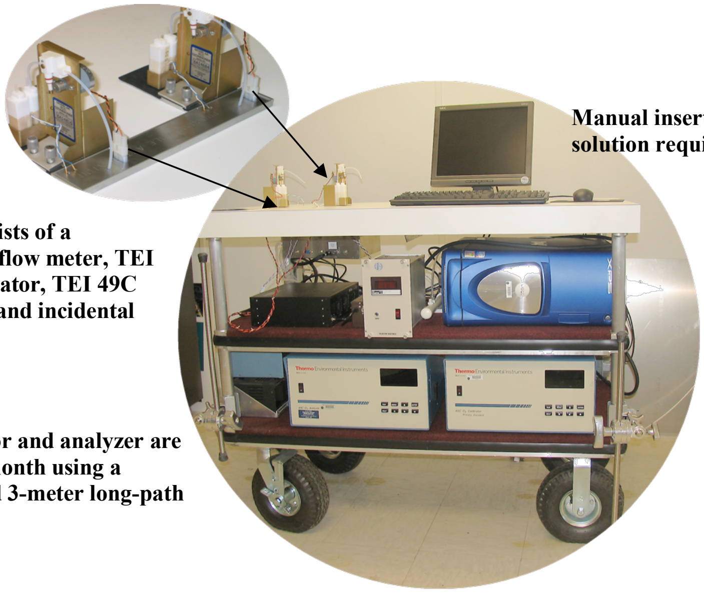
Fig05. Correlation between SPC 6A ECC ozonesondes and UV photometer measurements obtained during the BESOS mission: a) 1.0 percent KI solution, and b) 0.5 percent KI solution.

Fig06. Average ozone profiles from 12 pair of SPC 6a ECC ozonesondes indicating, at the 22 hPa pressure level, that the (0.5%,0.5B) ECCs' measured 7-8 nb less ozone, approximately 5 percent less, than the (1.0%,1.0B) ECCs'.

Fig07. Digital calibration bench results between (1.0%,1.0B) solution, blue curve, and (0.5%,0.5B) solution, red curve; the reference curve is shown in black.

Fig 01.

DIGITAL CALIBRATION BENCH

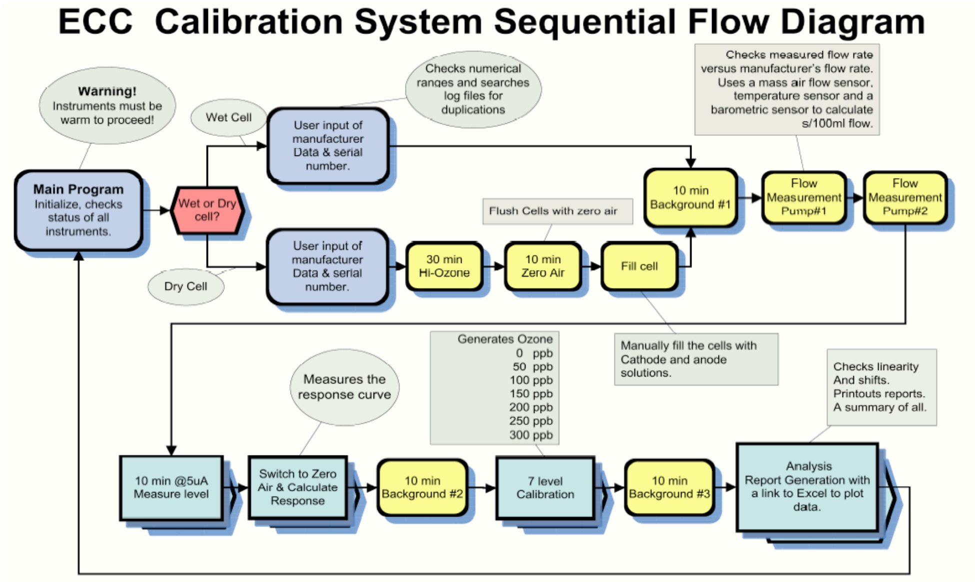


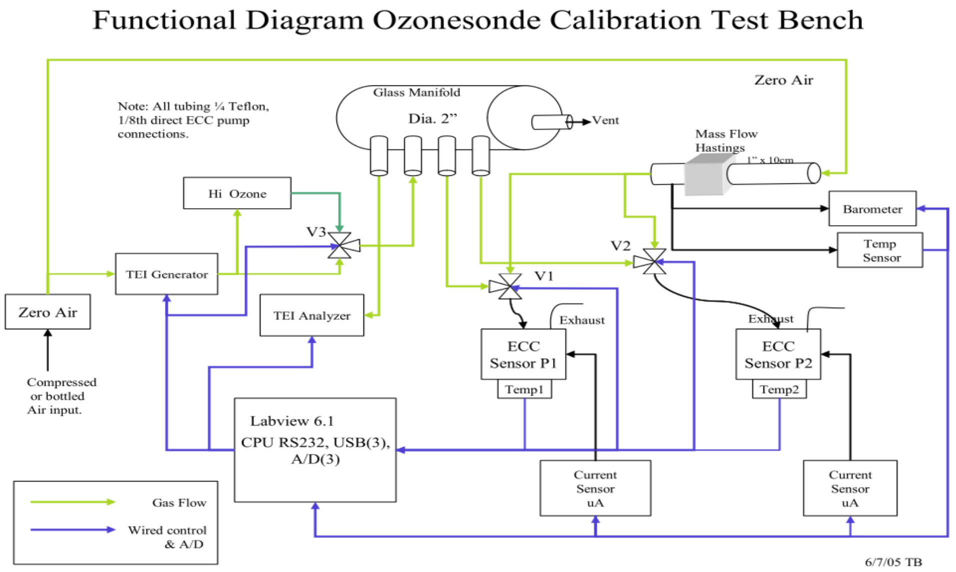
Manual insertion of KI solution required

The system consists of a computer, mass flow meter, TEI 49C ozone generator, TEI 49C ozone analyzer, and incidental equipment.

The TEI generator and analyzer are calibrated each month using a primary standard 3-meter long-path photometer.

Fig 02.


ECC Calibration System Sequential Flow Diagram
Warning! Instruments must be warm to proceed!
Main Program Initialize, checks status of all instruments.
Wet Cell
Wet or Dry cell?
Dry Cell
User input of manufacturer Data & serial number.
Checks numerical ranges and searches log files for duplications
User input of manufacturer Data & serial number.
30 min Hi-Ozone
10 min Zero Air
Fill cell
Flush Cells with zero air
Checks measured flow rate versus manufacturer's flow rate. Uses a mass air flow sensor, temperature sensor and a barometric sensor to calculate s/100ml flow.
10 min Background #1
Flow Measurement Pump#1
Flow Measurement Pump#2
Manually fill the cells with Cathode and anode solutions.
Generates Ozone 0 ppb 50 ppb 100 ppb 150 ppb 200 ppb 250 ppb 300 ppb
Measures the response curve
Checks linearity And shifts. Printouts reports. A summary of all.
10 min @5uA Measure level
Switch to Zero Air & Calculate Response
10 min Background #2
7 level Calibration
10 min Background #3
Analysis Report Generation with a link to Excel to plot data.


Functional Diagram Ozonesonde Calibration Test Bench
Zero Air
Note: All tubing ¼ Teflon, 1/8th direct ECC pump connections.
Glass Manifold
Dia. 2”
Vent
Mass Flow Hastings
1” x 10cm
Hi Ozone
V3
TEI Generator
Zero Air
TEI Analyzer
V2
V1
Barometer
Temp Sensor
Exhaust
Exhaust
ECC Sensor P1
Temp1
ECC Sensor P2
Temp2
Compressed or bottled Air input.
Labview 6.1 CPU RS232, USB(3), A/D(3)
Current Sensor uA
Current Sensor uA
Gas Flow
Wired control & A/D
6/7/05 TB

683 Fig 03.

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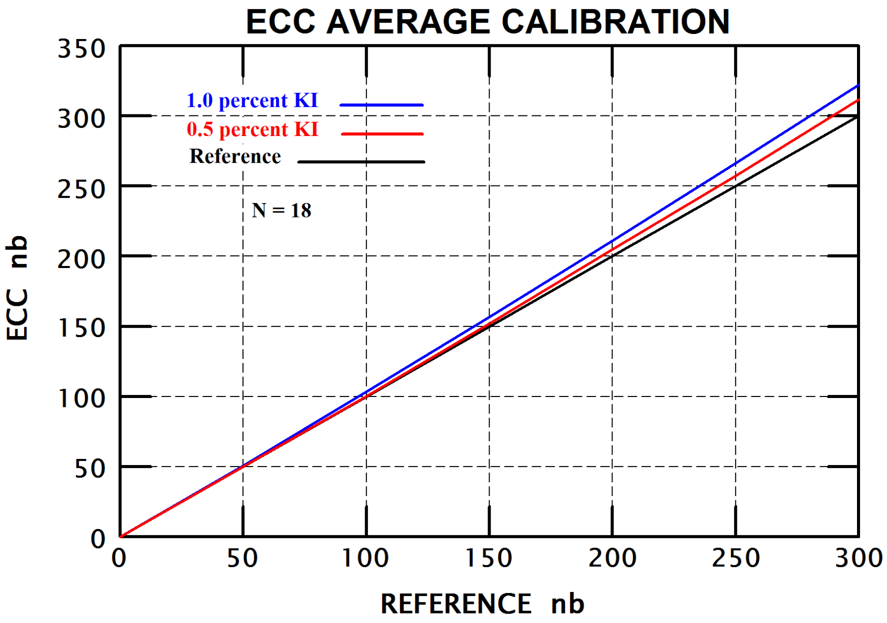


685

Fig 04.

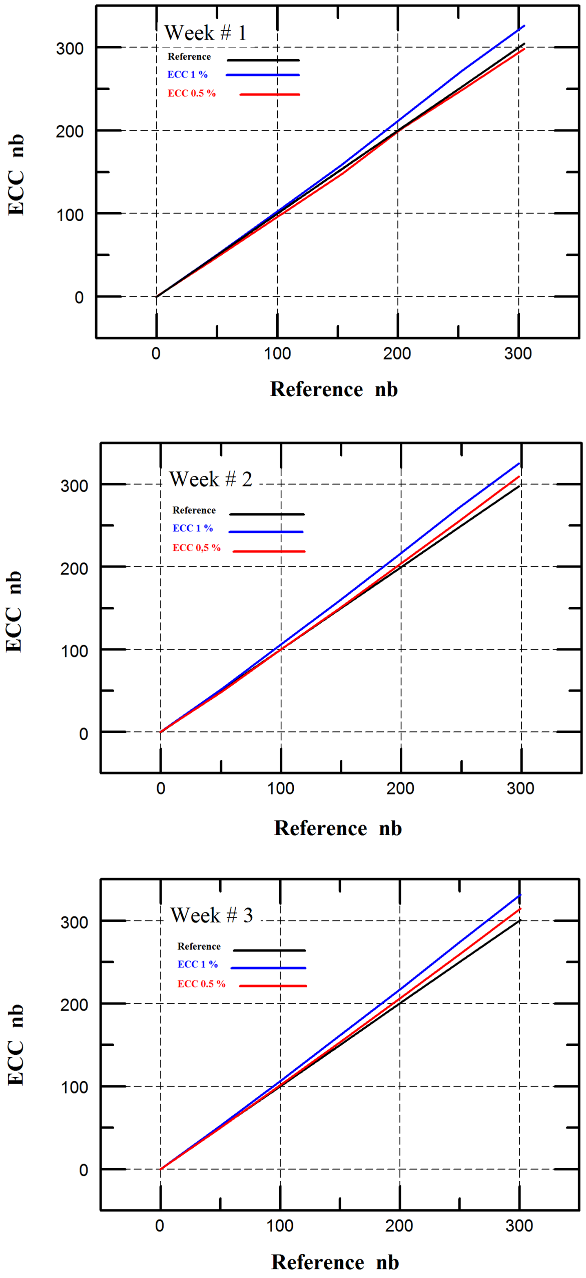

Week # 1
Reference
ECC 1 %
ECC 0.5 %
ECC nb
Reference nb
0
100
200
300
Week # 2
Reference
ECC 1 %
ECC 0,5 %
ECC nb
Reference nb
0
100
200
300
Week # 3
Reference
ECC 1 %
ECC 0,5 %
ECC nb
Reference nb
0
100
200
300

Fig 05.

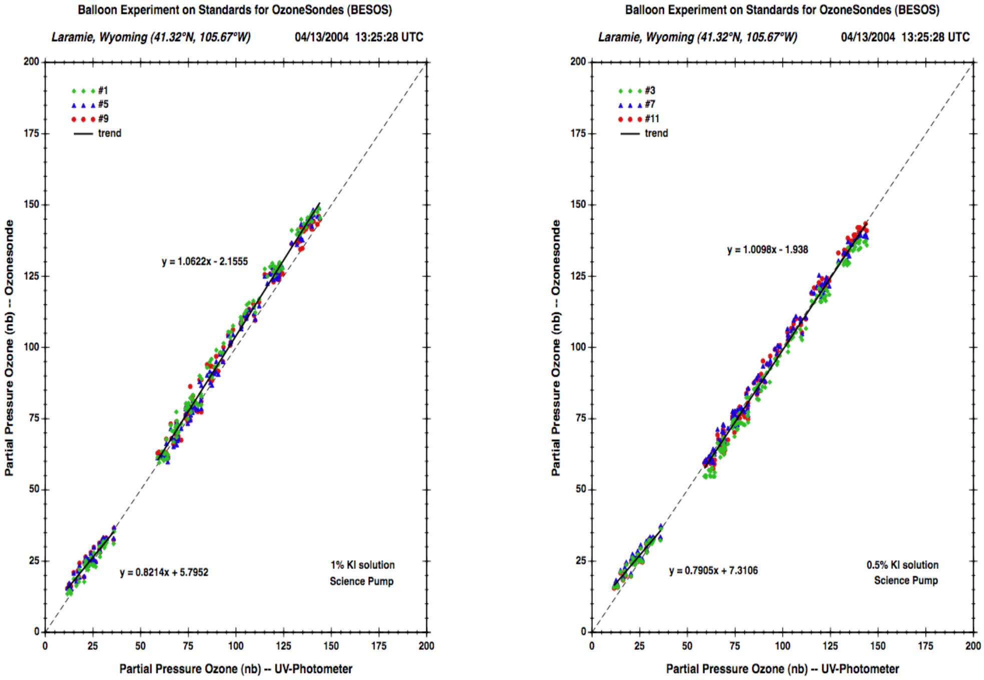

Balloon Experiment on Standards for OzoneSondes (BESOS)
Laramie, Wyoming (41.32°N, 105.67°W)
04/13/2004 13:25:28 UTC
● #1
▲ #5
● #9
— trend
y = 1.0622x - 2.1555
y = 0.8214x + 5.7952
1% KI solution
Science Pump
Partial Pressure Ozone (nb) -- Ozonesonde
Partial Pressure Ozone (nb) -- UV-Photometer
0
25
50
75
100
125
150
175
200
Balloon Experiment on Standards for OzoneSondes (BESOS)
Laramie, Wyoming (41.32°N, 105.67°W)
04/13/2004 13:25:28 UTC
● #3
▲ #7
● #11
— trend
y = 1.0098x - 1.938
y = 0.7905x + 7.3106
0.5% KI solution
Science Pump
Partial Pressure Ozone (nb) -- Ozonesonde
Partial Pressure Ozone (nb) -- UV-Photometer
0
25
50
75
100
125
150
175
200

Fig 06.

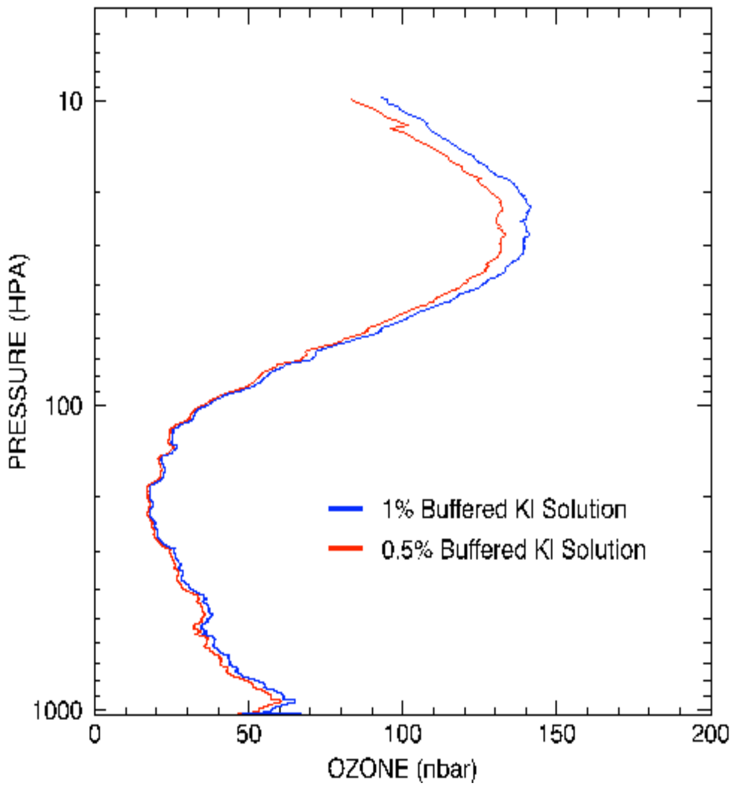
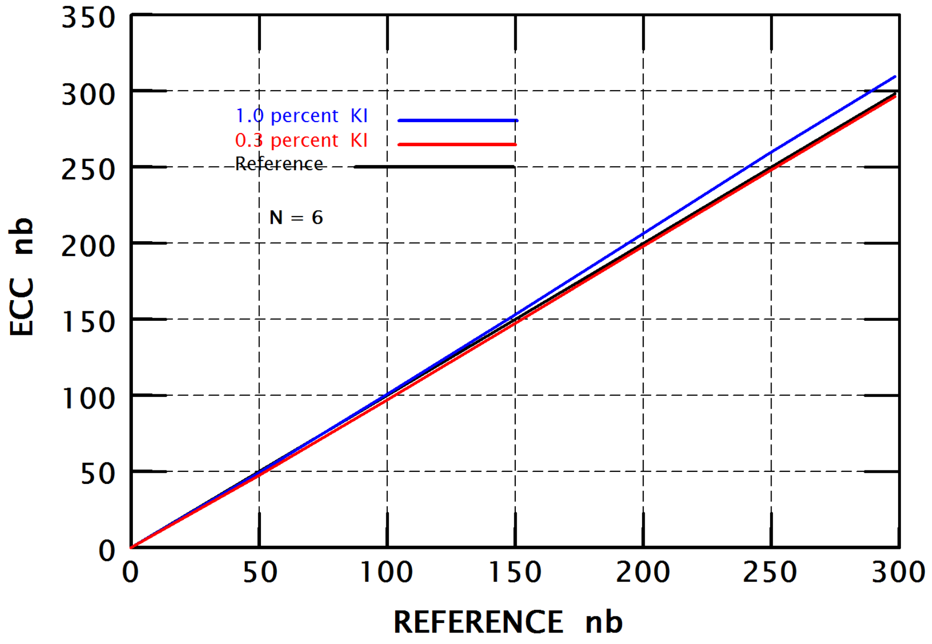

PRESSURE (HPA)
10
100
1000
0
50
100
150
200
OZONE (nbar)
1% Buffered KI Solution
0.5% Buffered KI Solution

Fig 07.


350
300
250
200
150
100
50
0
ECC nb
0
50
100
150
200
250
300
REFERENCE nb
1.0 percent KI
0.3 percent KI
Reference
N = 6