An Automated Method for Preparing and Calibrating Electrochemical Concentration Cell (ECC) Ozonesondes

Francis. J. Schmidlin[1] and Bruno A. Hoegger[2]

1) NASA/GSFC/Wallops Flight Facility; Wallops Island, Va. 23337 (Emeritus). E-mail: francis.j.schmidlin@nasa.gov
2) Bruno Hoegger Scientific Consulting; Marly, Switzerland CH1723. E-mail: hoegger.consulting@bluewin.ch

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 percent solution of potassium iodide (KI) and full buffer, show increasing partial pressure values when compared to the reference as partial pressures increase. Mean differences of approximately 5-6 percent are noted at 20 mPa. 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 percent cells. 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 conditions the ECC prior to flight and, if desired, 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 instrument types 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 dual balloon-borne ECC comparisons at Wallops Island. During implementation of the digital calibration bench, beta testing provided the ECC measurements used in this paper for demonstration purposes. Operational use at Wallops Island was intermittent and provided a limited number of calibrations between 2008 and 2017, when bench components began to fail.

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. Uncertainties arise from poor compensation for the loss of pump efficiency; erroneous background current; variable motor speed; solution loss from turbulent cathode cell bubbling; air flow temperature error and whether the temperature is measured at the proper location; and, inappropriate potassium iodide (KI) concentrations. Understanding the influence these parameters have on the ozonesonde measurement capability is particularly important. The digital calibration bench is able to measure these parameters over a range of partial pressures. 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. Tarasick et al (2016) provide a detailed discussion of ECC errors and the effect of these errors on resulting re-evaluated Canadian ozonesondes. Witte et al (2019), leveraging methods to homogenize ECC measurements based on Smit et al (2012), was able to reprocess 28 years of Wallops ECC data and provided uncertainties, However, efforts of the ASOPOS-team (Smit 2014) are especially notable for developing a standardized system of ECC procedures leading to enhanced ozonesonde usefulness. Although considerable effort is being expended to understand and improve ECC measurements we believe the use of a tool such as a digital calibration bench will further aid in removing much of the uncertainty.

2 Digital Calibration Bench Description and Operational Procedure

2.1 Description

The computer-controlled preparation and calibration bench fabricated at NASA Wallops Flight Facility was constructed using many of the features of a 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. The MeteoSwiss and Wallops digital calibration benches are functionally similar but are not identical in design, in fact, the MeteoSwiss bench is known as DigiBench. Also, a comparable bench that was furnished by MeteoSwiss to the meteorological station at Nairobi, Kenya has been operational for a number of years. The Wallops Island ozone site was interested in the digital bench because of its capability to provide detailed and repeatable preparation of ECC's; and, its automated feature requires less interaction with the ECC then the manual preparation method.

Throughout the history of ECC ozonesonde performance, the concentration of the KI solution has been questioned (Thornton and Niazy, 1982; Barnes et al, 1985; Johnson et al, 2002; Sterling et al, 2018). In the late 1960's and early 1970's the ECC used 2 percent KI solution in the cathode cell. In the mid-1970's the concentration was changed to 1.5 percent, and in 1995 the KI solution was changed once more to 1 percent. Employing the Wallops digital calibration bench would enable homogenization of the datasets obtained with the different concentrations and improve the reliability of the long-term database. The calibration bench accurately measures the ozone reaching the ECC cells while a TEI ozone generator provides the source of ozone at partial pressures from 0 mPa to 30 mPa. A second TEI instrument accurately measures the ozone sent to the ECC, providing a reference value. Thus, performance comparisons are possible without expending costly instruments.

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 (TEI Analyzer).

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 (0-30 mPa). 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 Thermo Electric Model 49C ozone analyzer. The analyzer contains the UV photometer that provides the reference partial pressure.

The digital bench reads the air flow from a Hasting Mass-Flow meter permitting a precise flow rate to be determined. The digital calibration bench uses the Hasting Mass-Flow meter model ENALU and a HS500m transducer with a maximum mass-flow of 500 scc/min. The mass-flow is converted to volume-flow by the conventional conversion formula. The volume flow rate measurement is comparable to the flow rate determined with a volumetric bubble flow meter. 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 is able to measure the time to less than 1 second. Tarasick et al (2016) point out that the operator uncertainty when reading the bubble flow meter is about 0.1-0.3 percent. Further, the manual method requires that the effect of moisture present 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. Calibration from 0 mPa to 30 mPa generally exceeds the nominal range of atmospheric ozone partial pressure. Calibration steps are in 5 mPa 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 that is then 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 (17 mPa) test, response test, second background current, linear calibration between 0 mPa and 30 mPa, and the final background current. As indicated in Fig. 2, upper panel, 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 solution 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 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 anode cell is filled first with a saturated KI solution followed, after a 10-minute delay, by filling the cathode cell with 3 mL of 1 percent 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 indicated above. The operator, after adding fresh solution 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 determined. The air flow is output in sec/100 Mr. 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.

Measuring the response of the ECC to ozone decay requires setting the ozone generator to produce 17 mPa 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 17 mPa of ozone is the reference level used to initiate the response test. After recording 17 mPa of ozone for 10 minutes 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, V1 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. From the detailed record the program selects five points (1, 2, 3, 5 and 10 minutes) successively to calculate the response of ozone decay that should be 80-90 percent lower than the reference of 17 mPa. 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 from 0 mPa to 30 mPa . Step changes begin with 0 mPa, followed by measurements at 5, 10, 15, 20, 25, and 30 mPa. Each step requires approximately 2-3 minutes to complete allowing time for the cell to respond to each step change. The linear calibration includes the reference measurement made simultaneously with the ECC measurement. After the upward calibration reaches the 30-mPa level the calibration continues downward. 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 should result in a potential cost saving as there would be no need to expend radiosondes, ECC's, and balloons. The testing with the digital calibration bench is limited to the ranges of pressures and temperatures at sea level but would be an imprecise representation in the upper altitudes.

3.1 Digital Calibration Bench (General)

Quasi-simultaneous testing of two ECC's is possible, enabling comparisons of different concentrations of KI solutions. Comparisons of 2.0-, 1.5-, 1.0-, and 0.5- percent KI concentrations were carried out on the digital bench. The ECC agreement became closer to the ozone reference value with lower KI solution concentration. An earlier paper by Johnson et al (2002), using SPC and EnSci ECC's, demonstrated similar changes occur when testing various solution concentrations that included varying amounts of buffer. 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 here.

During the checkout of the digital calibration bench ECCsondes were calibrated in pairs and included different KI solutions. Tests indicated the pressure and vacuum measurements were nominal, some insignificant variation occurred but was not a cause for concern. Pump temperatures, controlled by the room air temperature, generally varied 0.1º C to 0.2º C, but in some cases as much as 1º C to 2º C . Motor currents showed some variation, some measured over 100 mA, suggesting a tight fit between the piston and cylinder. For example, one ECC motor current initially was 100 mA, a second measurement a week later the reading was 110 mA, a final reading after running the motor for a short time was 96.5 mA. 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 about 0.04 µA. Final background currents obtained prior to balloon release were in the range 0.01 and 0.02 µA. Finally, the response of all the cells fell to the necessary 80 percent decrease within less than one minute. Graphically checking a small sample of high-resolution responses found some small variation as ozone decreased. The linear calibration (0-30 mPa), 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 percent KI solution with full buffer (1.0%,1.0B and the second with 0.5 percent KI with one-half buffer (0.5%,0.5B). Conditioning of the ECC's followed the steps given in Fig. 2, upper and lower panels. In the stratosphere, ozone partial pressures usually range from 15 mPa to 20 mPa. Linear calibrations to 30 mPa are obtained, although a lower range may be reprogramed.

Figure 3 is a graphical example of differences between the reference ozone measurement and the measurements of (1.0%,1.0B) and (0.5%,0.5B) KI concentrations. A sample of 18 digital bench measurements were averaged representing the differences between two KI solutions. Standard deviations are shown on the data curves, however, the close proximity between the curves render the standard deviation lines too small to be useful; they also overlay each other to some extent. Thus, for clarity the standard deviations have been added as text in the figure. The standard deviations, although relatively small indicate there is greater variability with the (1.0%,1.0B) KI solution. Although Fig. 3 suggests that the two concentrations measured similar amounts of ozone between 0 mPa and 8 mPa, however, the difference between the ECC measured ozone and with the reference ozone is approximately 0.4-0.5 percent. Both curves begin to separate and diverge above 8 mPa. The averaged data at 10 mPa indicate that (1.0%,1.0B) is 0.34 mPa, or 3.4 percent higher than the reference and (0.5%,0.5B) is 0.05 mPa, or 0.4-0.5 percent higher; at 15 mPa the difference is 0.71 mPa, or 4.8 percent and 0.23 mPa or 1.5 percent higher, respectively; at 20 mPa the (1.0%,1.0B) KI solution is 2 mPa, or 6 percent higher than the reference and (0.5%,0.5B) is 0.48 mPa or 2.4 percent higher. A check at the 30-mPa level indicates the (1.0%,1.0B) solution is 7.8 percent above the reference and (0.5%,0.5B) is 3.6 percent above. These results identify the ECC with (0.5%,0.5B) KI concentration to be closer to the reference than the (1.0%,1.0B) KI solution . Both ECCs' partial pressure curves have a slope greater than 1 trending toward higher amounts of ozone when compared to the reference value as the partial pressure increases. It can be noted in the figure by the slopes of the data curves that the (1.0%,1.0B) KI measured ozone increases at a faster rate than the (0.5%.0.5B) measurement. Johnson et al (2002) have explained the effect of different KI solution concentrations in some detail as well as the side effects from the buffers used. The intent of the example is merely illustrative of the advantage provided by the digital bench for examining ECC behavior. At 5 mPa the two concentrations are separated 2.1 percent and at 30 mPa the separation is 3.9 percent, or in terms of a ratio between the two solutions 0.961 to 0.979. At 20 mPa the ratio is 0.966. Referring to the SPC ozonesondes compared during BESOS, Deshler et al (2017, Fig.5 and Table 2) indicate non-linearity between the (0.5%,0.5B) and (1.0%,1.0B) KI solutions had similar ratios of approximately 0.960 to 0.970.

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 balloon comparisons. Unfortunately, sea level calibrations cannot provide knowledge of ECC behavior under upper altitude 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 is characteristic of other 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 mPa to 30 mPa, was carried out, but only the calibration for 30 mPa is discussed. During the first week, Fig. 4a, the (1.0%,1.0B) KI solution was approximately 2.1 mPa, or 7 percent higher than the corresponding reference value. The (0.5%,0.5B) KI solution was about 0.6-0.7 mPa 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 2.7-2.8 mPa or 9 percent higher (approximately 0.6-0.7 mPa higher than during week one), while the ECC with the (0.5%,0.5B) KI solution was now 1.2 mPa 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 0.2 mPa and was now about 3.0 mPa, or 10 percent higher than the reference. The ECC with (0.5%,0.5B) KI increased an additional 0.1 mPa and now was 1.3 mPa or 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 should be expected that carrying out the preparation process 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 the possibility of impurity residuals present on the ion bridge. On the other hand, the changes could simply be a normal evolution of typical ECC performance behavior.

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 correspondence with the reference suggests that adjustments should be applied to each curve. After obtaining a large sample of similar digital bench measurements it should be possible to design a table of adjustments relative to ozone partial pressure useful for adjusting ozonesonde measurements. However, since the calibrations are made at sea level such an adjustment table would not be able to account for the influence of upper 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 simple to use and provides calibrations that include useful reference values, and is complementary to other methods, such as employed in the Jülich Ozone Sonde Intercomparison Experiment (Smit et al, 2007).

In the 1998-2002 period the Wallops ozone station released 12 pairs of dual-ECC balloons, successfully providing 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 comprised an ECC with (1.0%,1.0B) and an ECC with (0.5%,0.5B) KI solutions. The profiles were average and are displayed in Fig. 5. It can be noted that the mean (0.5%,0.5B) solution measures less ozone than that of the (1.0%,1.0B) KI solution. A similar relationship is seen in Fig. 3 and Fig. 4 . Fig. 5 shows the maximum ozone level to be about 14 mPa near 22 hPa, where the (0.5%,0.5B) KI solution measured approximately 1 mPa, or 5.7 percent less ozone than the ECC with the (1.0%,1.0B) KI concentration. This difference is larger than the result given by the digital calibration bench results of Fig.3, where, at 15 mPa, the difference between the ECC 1 percent KI and ECC 0.5 percent is 3.3 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 using a solution of 0.3 percent KI with one-third buffer (03%,0.3B). Six sets of ECC's were calibrated. Each 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, however, the lower (0.3%,0.3B) concentration was nearly equal to, or slightly less than the reference. Average values and standard deviations derived from the six tests are shown in Fig. 6. The standard deviations appear to be large compared to those of Fig. 3, but not unexpected considering the sample size is only six pairs. 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, between 2005-2007 a facility designated as the digital calibration bench was fabricated at NASA Wallops Flight Facility. 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 that included associated reference values. Tests conducted with the digital bench were performed under identical environmental conditions eliminating the expense and time associated with making similar tests in the atmosphere.

During initial implementation of the digital bench calibrations of ECC's prepared with (1.0%,1.0B) KI solution were carried out over a range of partial pressures from 0 mPa to 30 mPa. Comparison between ECC's with (0.5%,0.5B) and (1.0%,1.0B) KI solution and simultaneously obtained reference ozone values revealed the two KI solution strengths were measuring more ozone than the reference. The difference between the ECC's measured ozone partial pressures and the reference partial pressures increased at a different rate as the partial pressure increased. For example, the (1.0%,1.0B) measurements slope upward to increasingly larger differences with the reference ozone measurements, i.e., increasing from 4.8 percent higher partial pressure at 15 mPa (Fig. 3) to about 7.8 percent higher at 30 mPa; the (0.5%,0.5B) measurements slope from 1.5 percent to 3.6 percent higher than the reference.

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 about 4-5 percent for the 0.5 percent solution.

Results from the digital bench also corroborate the differences found between SPC 6A ECC'c flown on dual-instrument flights at Wallops Island. At a pressure of 22 hPa the dual flights showed the (0.5%,0.5B) ECC to be about 0.8 mPa lower than the (1.0%,1.0B) ECC, comparable to the mean difference at 20 mPa of 0.72 mPa (Fig. 3).

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 are simply examples of the digital bench utility. Furthermore, 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

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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 comparisons of ECC ozonesondes prepared with (1.0%,1.0B) [blue] and (0.5%,0.5B) [red] KI solution concentrations. The reference ozone curve is shown in black. Calibrations are made in 5 mPa steps from 0 mPa to 30 mPa.

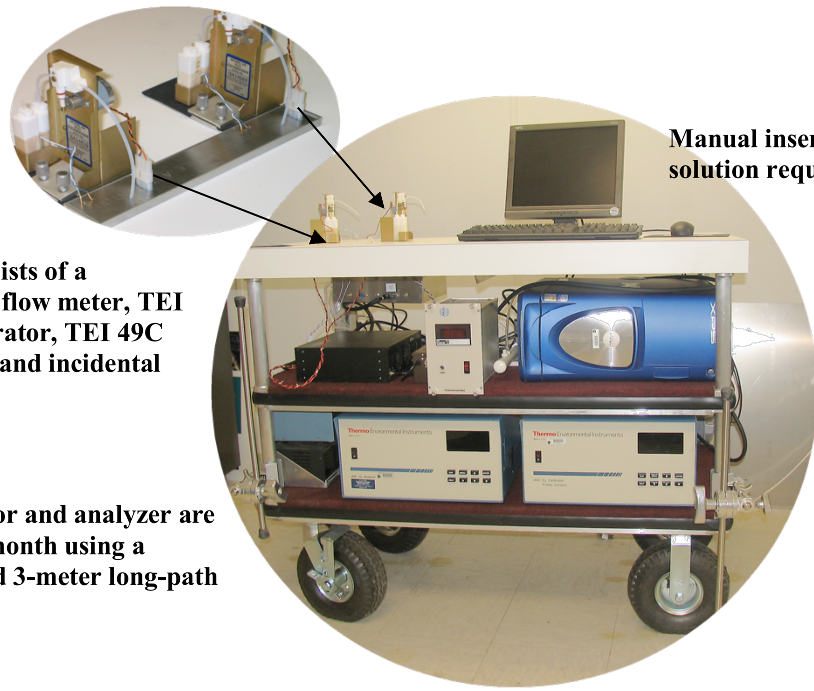
Fig04. Calibrations of two ECC ozonesondes, one using 1 percent KI solution and the other 0.5 percent KI, over a three-week period.

Fig05. 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 approximately 0.7-0.8 mPa less ozone or 5.7 percent less than the ECC's with (1.0%,1.0B) KI solution.

Fig06. Digital calibration bench results between (1.0%,1.0B) solution, blue curve, and (0.3%,0.5B) solution, red curve; the reference ozone curve is shown in black.

Fig 01.

DIGITAL CALIBRATION BENCH

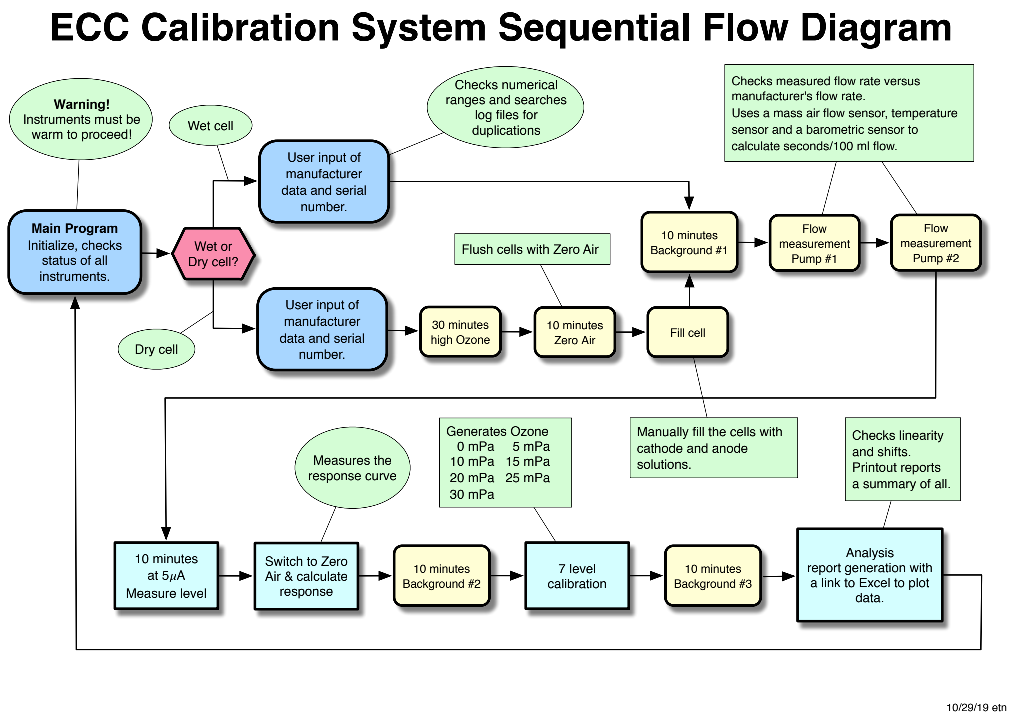


Manual insertion of KI solution required

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!
Wet cell
Checks numerical ranges and searches log files for duplications
Checks measured flow rate versus manufacturer's flow rate. Uses a mass air flow sensor, temperature sensor and a barometric sensor to calculate seconds/100 ml flow.
User input of manufacturer data and serial number.
Main Program Initialize, checks status of all instruments.
Wet or Dry cell?
Flush cells with Zero Air
10 minutes Background #1
Flow measurement Pump #1
Flow measurement Pump #2
User input of manufacturer data and serial number.
Dry cell
30 minutes high Ozone
10 minutes Zero Air
Fill cell
Measures the response curve
Generates Ozone 0 mPa 5 mPa 10 mPa 15 mPa 20 mPa 25 mPa 30 mPa
Manually fill the cells with cathode and anode solutions.
Checks linearity and shifts. Printout reports a summary of all.
10 minutes at 5μA Measure level
Switch to Zero Air & calculate response
10 minutes Background #2
7 level calibration
10 minutes Background #3
Analysis report generation with a link to Excel to plot data.
10/29/19 etn

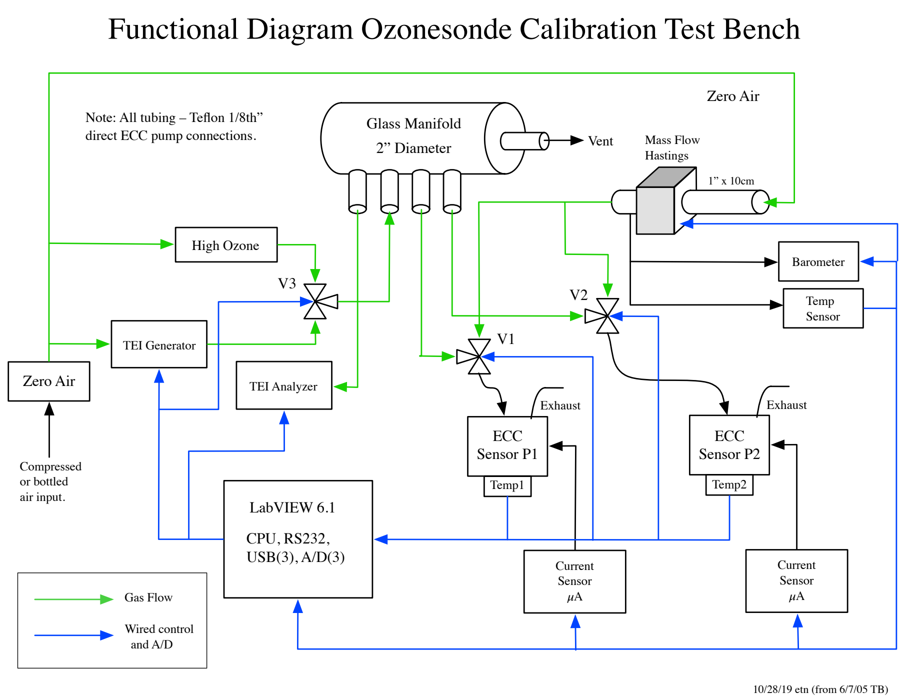

Functional Diagram Ozonesonde Calibration Test Bench
Note: All tubing – Teflon 1/8th" direct ECC pump connections.
Glass Manifold 2" Diameter
Vent
Zero Air
Mass Flow Hastings
1" x 10cm
High Ozone
V3
Barometer
Temp Sensor
V2
V1
TEI Generator
Zero Air
TEI Analyzer
Exhaust
Exhaust
ECC Sensor P1
ECC Sensor P2
Temp1
Temp2
Compressed or bottled air input.
LabVIEW 6.1
CPU, RS232, USB(3), A/D(3)
Current Sensor μA
Current Sensor μA
Gas Flow
Wired control and A/D
10/28/19 etn (from 6/7/05 TB)

Fig 03.

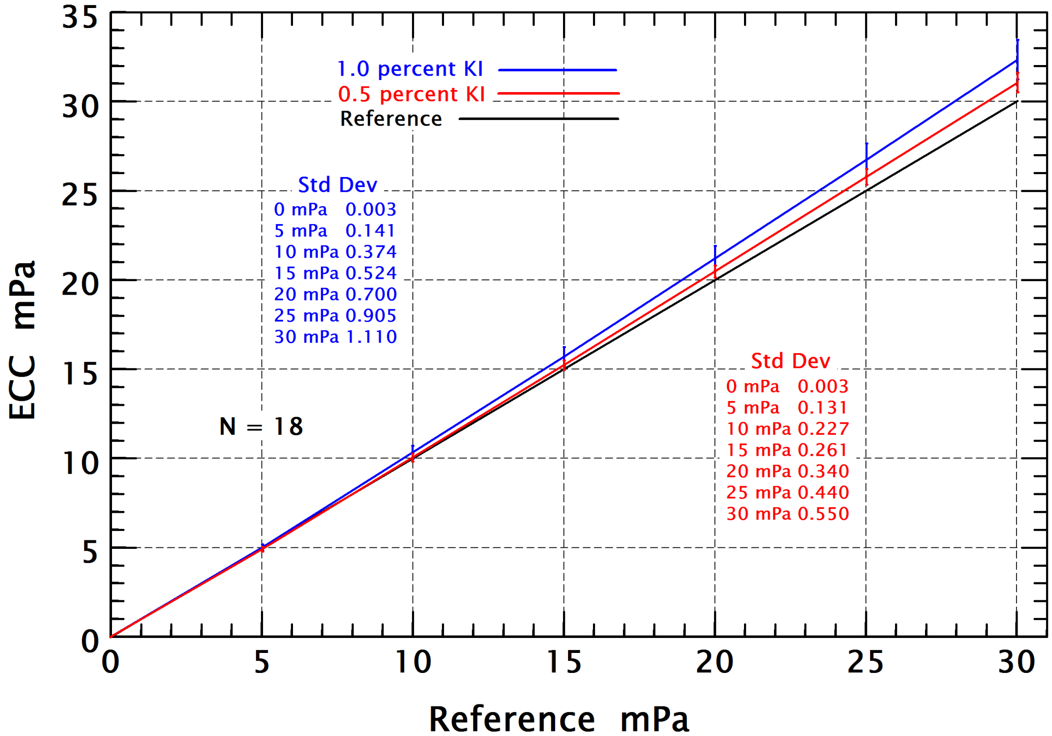

1.0 percent KI
0.5 percent KI
Reference
Std Dev
0 mPa 0.003
5 mPa 0.141
10 mPa 0.374
15 mPa 0.524
20 mPa 0.700
25 mPa 0.905
30 mPa 1.110
Std Dev
0 mPa 0.003
5 mPa 0.131
10 mPa 0.227
15 mPa 0.261
20 mPa 0.340
25 mPa 0.440
30 mPa 0.550
N = 18
ECC mPa
Reference mPa
0
5
10
15
20
25
30
35

Fig 04.

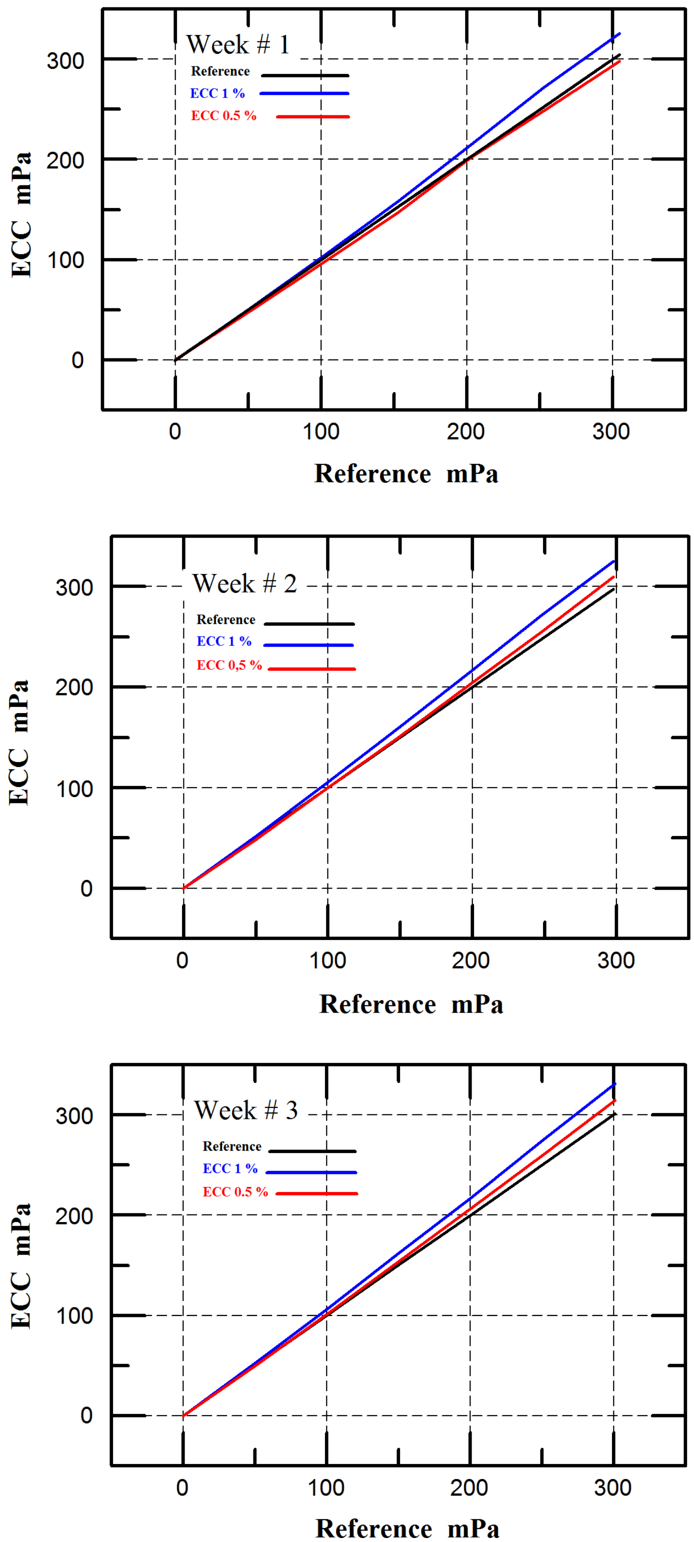
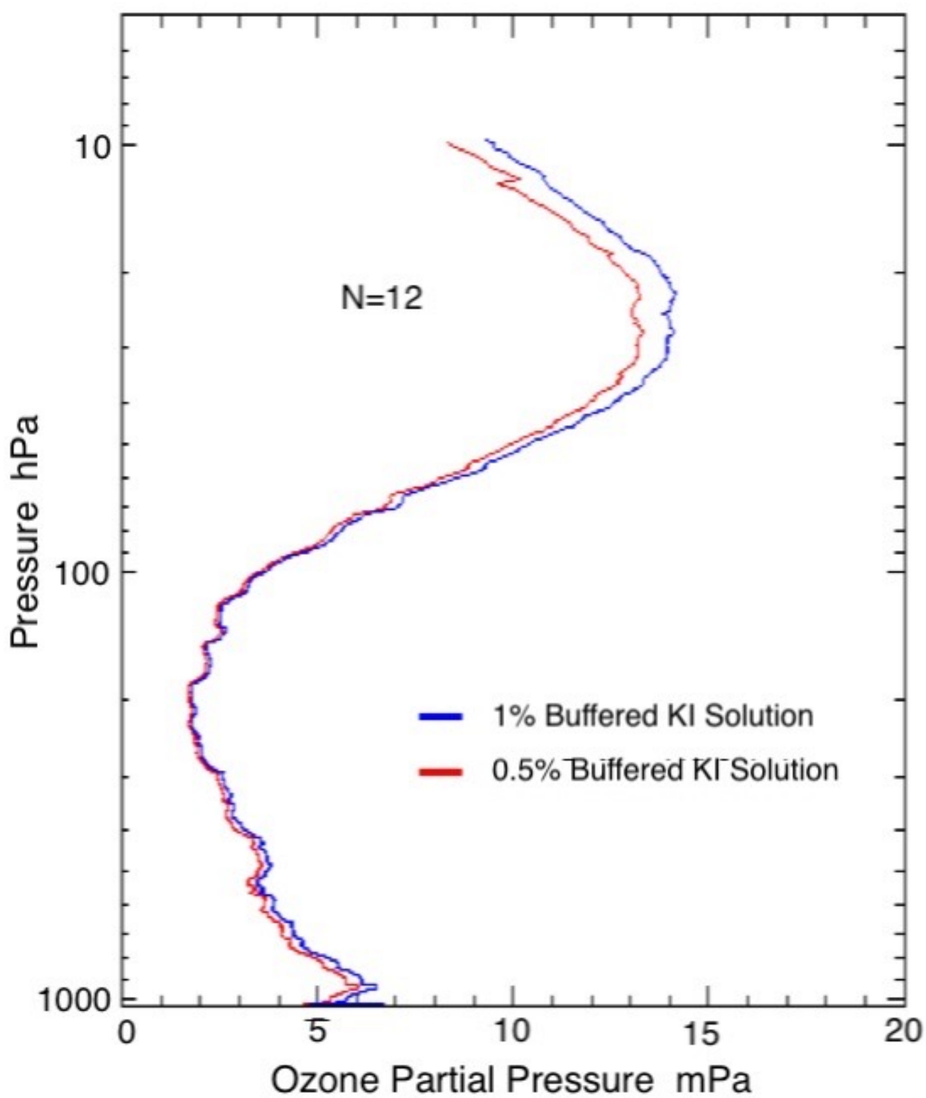
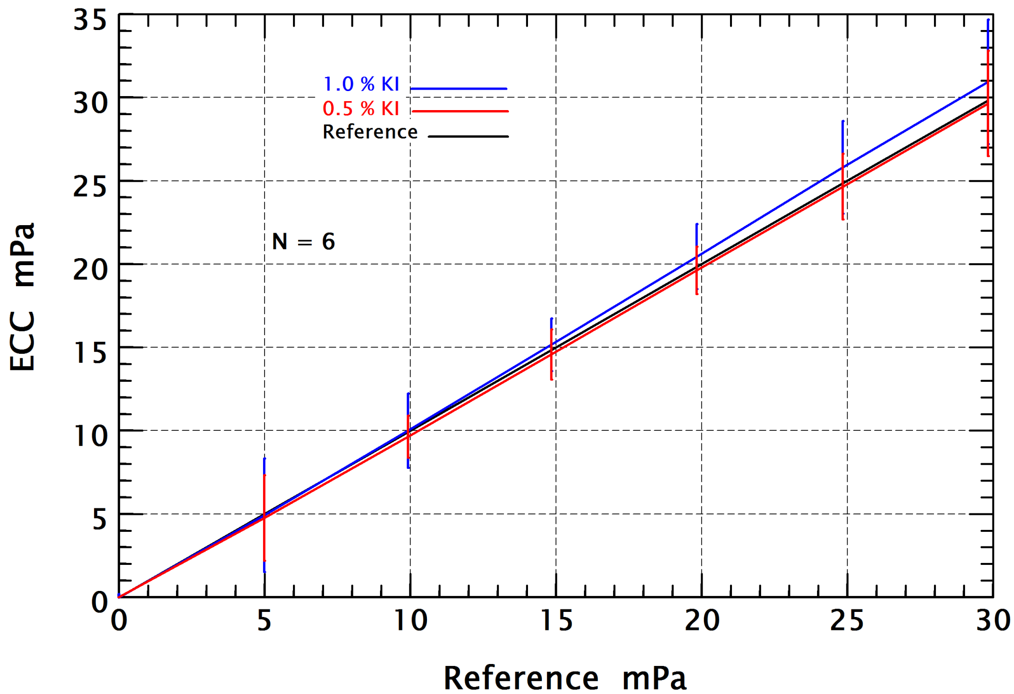

Week # 1
Reference
ECC 1 %
ECC 0.5 %
ECC mPa
Reference mPa
0
100
200
300
Week # 2
Reference
ECC 1 %
ECC 0,5 %
ECC mPa
Reference mPa
Week # 3
Reference
ECC 1 %
ECC 0.5 %
ECC mPa
Reference mPa

Fig 05.



N=12
1% Buffered KI Solution
0.5% Buffered KI Solution
Pressure hPa
10
100
1000
0
5
10
15
20
Ozone Partial Pressure mPa

Fig 06.


1.0 % KI
0.5 % KI
Reference
N = 6
ECC mPa
Reference mPa
0
5
10
15
20
25
30
35