Measurements of the Electrical Conductivities of Air over Hot Water

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ABSTRACT

Measurements of the conduction current between two electrodes in air over recently boiled water have been interpreted by Carlon as indicating that the humidified air became highly conductive and that large numbers of ions were produced in the air after it was saturated with water vapor. These interpretations have been questioned because it is possible that the insulators used in the high-humidity experiments allowed leakage currents to flow and these were treated as though they were conduction currents through the air.

We repeated these measurements with the use of a conventional, Gerdien cylinder conductivity-measuring apparatus that had insulators heated to temperatures above the dew point of the water vapor in the air being measured so that the insulators maintained high resistances. The results from the heated Gerdien cylinder experiments contradict the suggestions of high conductivities in humid air, for the measured conductivities of air were repeatedly observed to *decrease* by about 50% when recently boiled, hot water was brought in contact with the air.

1. Introduction

In a recent communication, Vonnegut and Mohnen (1987) have questioned the electrical conductivity estimates for humid air reported by Carlon (1979, 1980, 1981, 1982, 1983). Carlon has measured the conduction currents between two electrodes supported by Teflon insulators in air above recently boiled water and has treated the currents as though they all had flowed through the air between the electrodes, having been carried by ions in the air. He maintained that any conduction currents flowing between the electrodes through the Teflon supports were negligible (Carlon, 1983), but this assumption has been questioned by Vonnegut and Mohnen for the conditions with high humidities.

From his conduction measurements, Carlon has inferred that air humidified by boiling water contains abnormally high concentrations of singly-charged ions. The measurements have been further interpreted by Carlon as indicating that the high concentrations of ions can be maintained in air saturated with water vapor for one hour or more after the boiling has ceased. He explained these ions as the decomposition products of water molecule clusters in the vapor and calculated the concentrations of the ions as being greater than 10^6 cm^{-3}. He has suggested (Carlon, 1982) that the processes producing ions in his apparatus may also be operative in the free atmosphere at normal temperatures so that "One would expect intensive ionic activity in clouds and fogs . . . ."

If the phenomenon reported by Carlon occurs within natural clouds, it should cause enhanced conductivities of the cloudy air as a result of the increased ion pair production rates. (This effect would be limited, however, by the ion removal processes which include attachment to cloud particles and ion recombination.) It is worth pointing out that a number of investigators have found that cloudy air, in the absence of other ionizing processes, is less conductive than is clear air under the same conditions. For example, Israel and Kasemir (1952) who measured the conductivities of the air at a mountain-top observatory, reported that when a cloud enveloped the mountain, the conductivities decreased to about one-third that found when the air was cloud-free. Rust and Moore (1974) measured the conductivities of cloudy air aloft away from the earth's surface, using a special, balloonborne Gerdien cylinder and found low values, of the order of 4×10^{-15}/ohm m or less with relaxation times in excess of 2000 seconds.

Profound changes would be required in our understanding of atmospheric electric phenomena if Carlon's findings were substantiated. It therefore appears desirable to repeat his experiment and to test his results by the use of the conventional conductivity-measuring

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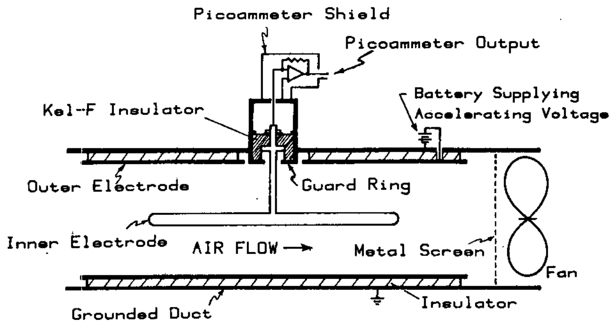

FIG. 1. Sketch illustrating the construction of a Gerdien cylinder.

equipment that has been developed over many years and has been found to be trustworthy by many investigators.

2. Instrumentation

The conventional equipment for measuring the electrical conductivity of a gas is a Gerdien cylinder (Gerdien, 1905; Swann, 1914; Tammet, 1967). As shown in Fig. 1, it consists of a conducting, cylindrical electrode within which is mounted coaxially an isolated, "T" shaped electrode. When the gas of interest is caused to flow in an axial direction through the open ends of the cylinder and an electrical potential difference is imposed between the two electrodes, ions in the gas between the electrodes will move under the influence of the electric field produced by the potential difference. Some of the ions having the same polarity as that of the surrounding cylinder will migrate under the imposed electric forces to the inner electrode and be collected there where they can be measured as a current flow with a picoammeter in the circuit. The electrical conductivity provided by one polarity of the ions in the gas can then be calculated from measurements of this current with the use of geometric factors of the apparatus and knowledge of the imposed potential difference (Chalmers, 1967). (The "polarity" of the conductivity that is measured is, of course, determined by the polarity of the applied potential difference.)

Significant errors can result if current flows directly from the electrified cylindrical electrode to the inner one across or through the mounting insulator that is required to support the inner electrode in this configuration. Any such "leakage" current will be added, in the measuring picoammeter, to the conduction current of interest and will cause an erroneous indication of high conductivities in the gas. To eliminate this source of error, modern Gerdien cylinders are equipped with a grounded, metallic "guard" ring around the insulator that supports the isolated electrode. This arrangement conducts any leakage current from the outer electrode directly to ground and shields the ion collecting, sensing electrode from its effect.

Undesired leakage currents can also flow between the guard ring and the sensing electrode when, for example, condensation of water vapor occurs and causes a conducting film to form on the surface of the insulator separating the guard ring from the sensing electrode. If the metals comprising the electrode and the guard ring are the same, the principal effect of this leakage can be a shunting of a portion of the ion current of interest to ground such that it is not measured in the picoammeter and the calculated value for the gas conductivity is smaller than the true value. If the two metals are electrochemically different, a voltaic cell can be established when they are connected by a water film. In this case, a spurious current may flow through the circuit comprised by the guard ring, the voltaic cell, the support for the sensing electrode, the picoammeter and ground. This would give rise to an erroneous indication of an increase in one polarity for the ionic conductivity of the gas coupled with a similar decrease in the measurement of the other ionic polarity.

To minimize the first of these leakage effects, the mounting insulators in all of our Gerdien cylinders are separated by grounded guard rings and the inner insulator in each is fabricated from a fluorinated polyethylene, Kel-F, which, in the absence of liquid water, has high volume resistivity and a surface resistance limited only by the resistance of the surrounding air. (Kel-F is less piezo-electric than is Teflon, the other available fluorinated polyethylene, but Kel-F is about equal to Teflon as an insulating medium for most uses and is the best insulating material available to us for these measurements.) The guard ring and the metal support for the sensing electrode have been machined from brasses of similar composition that show little electrochemical effect under high humidities. As described below, strenuous efforts have been made to keep the insulators dry.

Carlon designed his own conductivity cells in which no guard rings were used. His objections to Gerdien cylinders were based on their "modest dimensions and poor sensitivities". He also concluded that "Conventional ion counters such as Gerdien tubes do not work well near $s = 1$ (100% relative humidity) due to insulator leakage and very poor cell factors". On the other hand, in his view, "Teflon-insulator cells overcome these problems by obtaining good cell factors with compensation for insulator leakage, thus allowing measurements which previously could not be made".

With our Gerdien apparatus and a Keithly type 602, battery-operated electrometer, we can measure ion current differences of less than 10 fA reliably and repeatedly. Such an ion current would be produced in our apparatus with air having a polar conductivity of 8×10^{-16}/ohm m for an acceleration potential of 20 V so that lack of sensitivity is not a limitation in measuring the conductivity of the ambient air with this Gerdien equipment.

In our early tests, leakage occurred across the Kel-F insulator within the guard ring in our apparatus when water vapor with large supersaturations was forced to condense in this area. To prevent condensation in the Gerdien cylinder during our measurements reported here and to meet Carlon's objections about insulator leakage in this apparatus, we have wrapped glass-cloth-insulated heating tapes around the outside of the outer cylinder and around the mount for the Kel-F insulator with the guard ring. An electrical input of about 90 watts into these tapes raised the insulator temperature above 100°C where it was maintained during the later measurements reported here.

3. Gerdien cylinder characteristics

When the apparatus, the applied potential and the air flow are arranged so that some (but not most) of the ions in the air passing through a Gerdien cylinder are collected during their passage, the polar conductivity, $\lambda_\pm$, of the air can be calculated from the Gerdien relation (Chalmers, 1967):

$$\lambda_\pm = (i*\epsilon)/(C*V_\pm),$$

where i is the ion current collected, ϵ is the permittivity of the air (8.85 pF/m), C is the electrical capacitance of the axial ion-collecting electrode, and $V_\pm$ is the applied potential difference. The measured capacitance of the axial electrode in our apparatus is 5.7 pF. (The ion-collecting electrode had a length of 20.4 cm and a diameter of 1.27 cm. The outer cylindrical electrode had an internal diameter of 9.65 cm.)

The potentials applied ranged from ±5.6 V to ±72 V. For our instrument, the ion current collected is directly proportional to the applied potential differences for values ranging from 5 to 25 V. Above 25 V, the instrument response begins to become non-ohmic as ion depletion effects develop and the device begins to act as an "ion counter".

Air is drawn through the outer cylinder at speeds of about 1 m s^{-1} by a "muffin" fan attached downstream to a grounded, metal duct that surrounds the electrified outer cylindrical electrode. A grounded, fine mesh metal screen (with openings of about 1 mm square) shields the ion-collecting electrode from electrical disturbances arising from the rotation of the fan blades.

4. Conductivity measurements

a. Measurements at room temperature

Initially, the Gerdien apparatus was set up and operated in a closed room where accelerating potential differences of ±20.0 V were applied to the outer electrode relative to the grounded terminal of the Keithley 602 electrometer used as a picoammeter. The output from the electrometer was recorded by a sensitive, strip chart oscillograph. Measurements of both polarities of the room air conductivity were made for several days to obtain values of the normal conductivities in the room. When the room was sealed, conductivities of either polarity as high as 7.5×10^{-14}/ohm m were repeatedly found; when the doors to the outside air were opened, the conductivities decreased rapidly to values of about 1.5×10^{-14}/ohm m. (These measurements indicated to our local radon expert, Professor Marvin Wilkening, that when the room was closed, low level radioactive gases were accumulated and increased the ion population in the room significantly.)

After steady-state ion collection was attained within the closed room indicating a positive conductivity of about 4.8×10^{-14}/ohm m, one liter of water from the city mains was brought to a boil in a metal beaker and then was placed 1 cm in front of the air intake to the Gerdien cylinder. The initial temperature of the water in this position was 90°C. (All of the apparatus was at room temperature [28°C] and the relative humidity of the air initially was less than 20%.) The indicated positive conductivity of the air quickly decreased by more than 50% and it remained at the lower values until the beaker of water was removed about 7 minutes later whereupon the conductivity increased to 3.7×10^{-14}/ohm m. The polarity of the accelerating voltage was then changed to negative and, after ion collection reached steady state, the experiment was repeated with boiling water, initially at 96°C. After the hot water was placed at the intake of Gerdien cylinder, the negative conductivity of the air decreased by about 20% and remained there until the water was removed, whereupon it increased back to about 4×10^{-14}/ohm m.

It is interesting to note that the air conductivities observed before the hot water was first brought into the closed room were higher than those found later. Even after the hot water was removed from the proximity of the Gerdien apparatus, the measured conductivities remained at values lower than the original ones until the air in the room was changed by opening the doors. An extract from the recording of this early test is shown in Fig. 2.

No condensation of water was observed anywhere on the apparatus during its exposure to the hot water and none was expected in view of the low relative humidity in the room. We doubt, therefore, that the decrease observed in the ion current collected was due to a wetting of the insulators by condensation of water vapor.

This simple experiment was performed to identify any immediate or gross effects caused by the addition of water vapor and it indicated no enhancement in the population of fast ions in the room-temperature air that passed over hot water on entering the Gerdien cylinder. One explanation for the observed decreases in the conductivity of the moistened air is that the added water molecules caused increases in the sizes of the ions existing in the previously dry air, thereby decreasing their mobilities on which the conductivity depends.

b. Measurements made with a heated Gerdien cylinder

In an effort to measure the conductivity of air saturated with water vapor, the Gerdien apparatus with

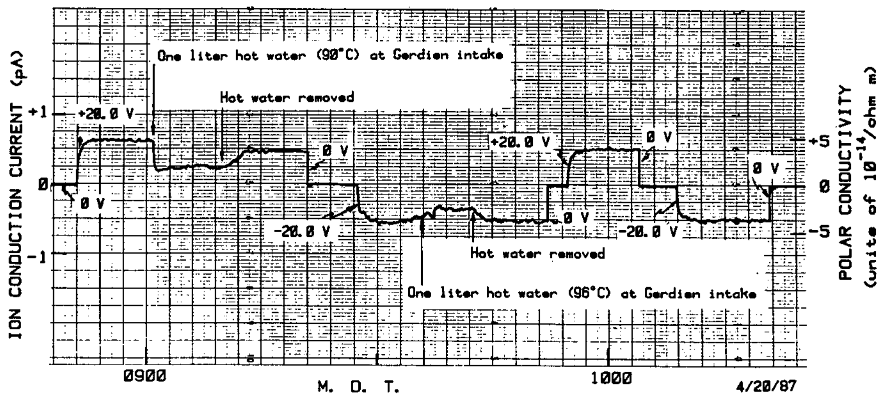

FIG. 2. Recording of the ion collection current in a Gerdien cylinder at room temperature during periods when a beaker of hot water was placed in front of the Gerdien intake and then removed. During this recording, the applied voltage was varied from zero to +20.0 to zero to −20.0 to zero and so on in order that both polarities of electrical conductivity could be calculated.

heating tapes was mounted on the side of a "vapor-tight", cubical aluminum box, 70 cm on a side. The air exhausted from the muffin fan was led through a flexible, aluminum covered duct, 7.6 cm in diameter and 2.5 m in length, to an inlet port in the side of the box about 65 cm distant from the Gerdien intake. Thus, the air drawn through the conductivity-measuring equipment was recirculated into the closed box and it had no contact with the outside air. A grounded aluminum pan was placed on thermal insulators just above the bottom of the box in front of the Gerdien intake. A Teflon tube, 13 mm inside diameter, was connected to the pan bottom from a funnel outside the box in such a manner that hot water could be introduced into the pan within the closed box quickly and without splashing. This arrangement of the equipment is shown schematically in Fig. 3 and a photograph of it is shown in Fig. 4.

The box was first sealed, the muffin fan and the heating tapes were energized and measurements were made of the polar conductivities over the next day using a 20.0 V applied potential, the polarity of which was reversed at intervals. Initially both conductivities of the air were about 3×10^{-14}/ohm m but, after 15 hours, they had decreased to values of about 1×10^{-14}/ohm m. (During this entire series of measurements, the temperature of the Gerdien insulator and guard ring was maintained above 102°C by the heating tapes.)

Four liters of hot distilled water, boiled at 96°C for the last hour, were then quickly introduced into the box through the Teflon tube. (The box temperature was initially about 28°C; after 1 hour, it rose to 48°C.) Immediately after the introduction of the hot water into the box, the conductivities of the recirculating air decreased to less than 5×10^{-15}/ohm m and they remained at these low values until the box was opened to the room air about 60 minutes later. When outside air was admitted to the box, the measured air conductivities increased over the next 20 seconds to values of about 1×10^{-14}/ohm m which suggests that the indicated low conductivities during the presence of large water vapor concentrations were due to low ion mobilities and concentrations and not due to leakage across the Kel-F insulator despite the readily apparent condensation on the inside walls and floor of the box.

As a direct test of the hypothesis that the heated insulator had become wet and conducted some of the collected ion current directly to ground thus avoiding the picoammeter and giving a falsely low value for the air conductivity, a small piece of outdated polonium foil (with a residual activity of less than 100 microcuries) was introduced into the return duct by opening it briefly while the box was still closed and the Gerdien apparatus was indicating low conductivities, of about 1.6×10^{-15}/ohm m, for the humid air. Within 10 seconds, the ion current collected from the recirculated air began an increase and, over the next 5 minutes, rose to more than 300 times the initial value. The enhanced conductivity indications continued until the polonium was removed 10 minutes later, whereupon the indicated conductivity in the closed box decreased to 8×10^{-15}/ohm m within 5 minutes more.

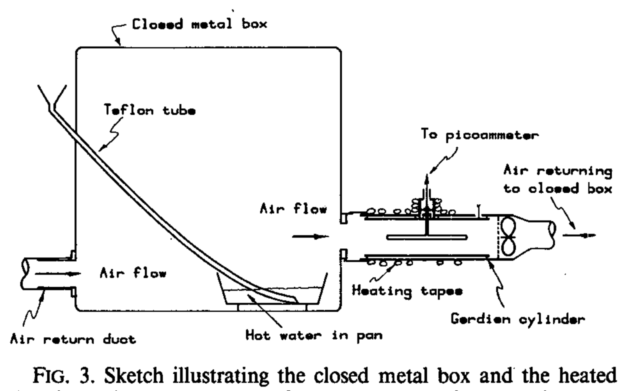

FIG. 3. Sketch illustrating the closed metal box and the heated Gerdien cylinder arrangement for measurement of the electrical conductivity of air over hot water.

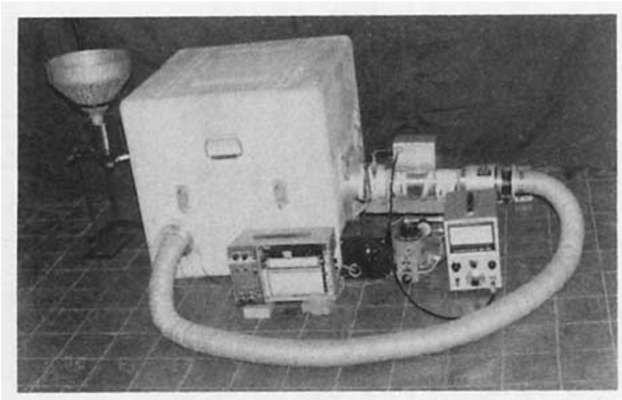

FIG. 4. Photograph of the closed box, the heated Gerdien cylinder, the electrometer and the strip-chart recorder used in the conductivity measurements.

The measurements with the heated Gerdien cylinder and the closed box were repeated nine times with variations that used distilled water, tap water, different voltages (from ±5.6 V to ±72 V) applied to the outer electrode, air of differing initial conductivities for periods of up to 2 hours, and an electrical immersion heater that boiled water within the closed box. Essentially the same results were observed in each experiment: After the box was closed, the conductivities of the air in the box decreased to about 1×10^{-14}/ohm m. When hot water was introduced into the box, the conductivities of the enclosed air decreased even more, to values around 5×10^{-15}/ohm m or smaller and remained at less than the initial (dry) values for more than one hour or until the box was opened. An example of the ion current recording made during one of these experiments is shown in Fig. 5. The "spikes" on this record should be ignored for they were caused by switching transients during changes in the accelerating voltages. There is also more variability in this recording; both of these effects were caused by the use of the higher recording sensitivities required for the lower conductivities that occurred with water vapor in the closed box.

5. Discussion

Heating the insulators to temperatures higher than the dew point of the water vapor associated with the introduced hot water appears to have maintained the high resistance values required of the insulation for the air conductivity measurements so that they were not vitiated nor enhanced by leakage of extraneous currents.

The sudden rise in the measured conduction current immediately following the insertion of the polonium shows that the heated Gerdien apparatus could detect increases in the air conductivities whenever they occurred. Contrary to the predictions by Carlon, however, no increases in the conduction currents through the air in the system were ever observed resulting from increases in the humidity of that air. Our findings are that the electrical conducting ability of the air within our measuring apparatus is invariably *decreased* by the introduction of large quantities of water vapor.

This phenomenon has long been known to occur in the free atmosphere: For example, a U.S. Navy meteorologist, Commander D. H. Minton, observed characteristic *decreases* in the electrical conductivity of the air one hour or more before the development of a fog at his station and formulated fog forecasting rules based on this phenomenon and other meteorological information (Serbu and Trent, 1958). Minton's observations were interpreted as indicating decreases in the numbers of atmospheric fast-ions as a result of their attachment to nearby aerosol particles that grew in size and ion collecting ability whenever the relative humidity increased sufficiently. His rules were useful, in some meteorological situations, by providing warnings of the growth of atmospheric particles, long before they became obstructions to vision.

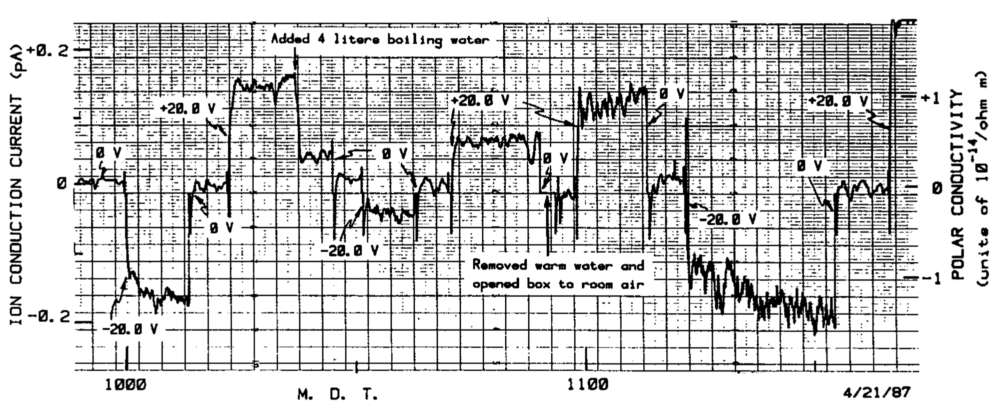

FIG. 5. Recording of the ion collection current in the heated Gerdien cylinder from air within the closed box before and after initially-boiling water was added. The voltages applied to the Gerdien electrodes were varied at intervals of about 6 minutes or more as in the measurements shown in Fig. 2.

Our results suggest to us that measurements of the electrical conductivities of humid air with conductivity cells that do not use guard rings and very dry insulators are of questionable validity.

The utility of a Gerdien apparatus as a simple monitor of the increases in atmospheric conductivity brought about by radioactivity was graphically demonstrated to us in this study. This suggests to us that the apparatus could be employed more widely as a simple monitor for the presence of abnormal amounts of radioactive substances affecting the local atmosphere.

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