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SIMULTANEOUS MEASUREMENTS OF OZONE CONTENT OF AIR NEAR THE EARTH
AT SEVERAL STATIONS BY MEANS OF A SIMPLE ABSOLUTE METHOD

Following is a translation of an address presented by Alfred Ehrert to a convention of the JGGU in Brussels on 30 August 1951. The address was published in the German language in the periodical Journal of Atmospheric and Terrestrial Physics, 1952, Vol 2, pages 169-195, Pergamon Press Ltd, London.

1. Abstract

The local ozone concentration of atmospheric air has been measured over a period at several stations by means of a chemical method which is simple in operation. Several characteristic series of results are given, clearly illustrating the destruction of ozone in the ground layer and the dominating influence of the exchange of air with higher layers. The method of measurement is briefly described.

2. Body of Address

Today, chemical methods are superior to optical methods for measuring the local ozone concentration in the atmosphere. Our method described below is particularly simple in operation because the inconvenient use of standard solutions is replaced by measurements of currents and their duration of connection and also because sufficient accuracy can be obtained with very small amounts of air. These features enable rapid operation. Operation of the devices requires no special experience in chemistry or special skills. Furthermore, the result contains only easily controlled standard quantities so that, even when using different apparatuses, absolute values capable of immediate comparison are obtained.

The above described features of our method encouraged us to equip several stations with these devices as a means of monitoring ozone near the surface of the earth over a wide geographical area.

Illustration 1 shows the locations of the monitoring stations. Arosa, where Mr Götz and Mr Volz carried out the measurements, was the highest station at 1900 meters. Mr Daubert of the Württemberg-Hohenzollern Weather Service performed the measurements at Tübingen. In Freiburg Mr Person (Baldenweger Hof) did the measurements. He is a member of the Südbaden Weather Service. Mr Busse, of the same weather service, took care of the stations in St. Blasien and Staufen in the Black Forest. At Bad Tölz, Mr Ungeheuer of the Climatological Station of the Weather Service of the US Zone of Occupation carried out the measurements.

The exact meteorological data obtained will be made public elsewhere. Here only several characteristic cases from this material will be discussed. I express my thanks to the several gentlemen involved in making the measurements for the data they have made available to me. The actual values from Arosa have been re-computed to the air pressure of the other stations with a mean factor for purposes of comparison.

First we see in Illustration 2 a cyclonic distribution with gusty winds from the west. In Arosa, the ozone values are 20% higher. The winds abated on 28 April 1950 and the ozone content dropped in Tübingen. The measuring station there is located in a castle about 20 meters above the rooftops of Tübingen and is exposed to westerly winds.

Illustration 3 shows the following period during which the weather at Tübingen was cool with light winds and overcast skies. The air mass above the city of Tübingen lost much of its ozone and there was little movement of fresh air into the area from greater altitudes. In Arosa the influences of the ground are much less and are effective only when air is transported over the city and the monitoring station from the valley, such as on 3 May 1950.

Illustration 4 shows a similar transition period from west winds to stagnated conditions at Tübingen. The weak thermic currents in the fall season are not sufficient to provide a full connection with the higher layers which are not influenced by the earth's surface.

In Illustration 6 we see the same thing again. The nightly increases on 19 and 20 July in Staufen and Tübingen are caused by turbulence in connection with storms.

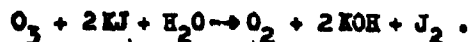
Illustration 7 shows that, given overcast skies and no wind in Tübingen during the winter season, there is sometimes no trace at all of the ozone which was already afloat in Arosa. The heated gases of the city create a visible smog overhead during such weather and rapidly destroy the ozone.

Finally, Illustration 8 depicts an unusual case wherein Arosa has less ozone than Tübingen or Baldenweger Hof near Freiburg in Breisgau. Here, on 17 January 1951 under a pronounced inversion (at 2000 meters), a new mass of ozone-rich air moved in, while Arosa and St Blasien were still under the old, ozone-poor air mass.

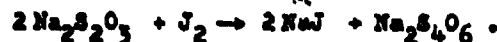
These findings clearly confirm the theory that ozone is rapidly destroyed on the surface of the earth (1), (2) and demonstrate once more (3), (5) that ozone, as a more or less reliable component of an air mass, can give important meteorological conclusions. However, measurements should not be made in cities on at ground level, but in the free atmosphere. The measurements which we made some time ago from aircraft yielded important basic data despite their small number (4), (5).

The method of measurement which we developed has already been publicized (6). In the two years since this publishing, further simplifications have been achieved, the mention of which would seem to be appropriate at this time.

Like many other authors, we used the oxydation of potassium iodide by ozone in neutral solution



Air is drawn through 3 cm³ of a 2% KI-solution in small bubbles. Also added to the solution is Na₂S₂O₃ which reacts immediately with the iodine resulting from the oxydation:



The oxydation of KI through ozone causes a loss of sodium thiosulphate. This we then measure and thus are able to determine the amount of ozone which was drawn in. This detour via the sodium thiosulphate is necessary because free iodine I₂ is removed from the solution by the air stream. Sodium thiosulphate does not suffer this loss.

Illustration 9 shows the reaction vessel developed for this purpose. From a reservoir of 2% KI solution with a sodium thiosulphate additive (approximately 1 cc n/100 to 750 cc KI solution), exactly 3 cc are placed into the glass receptacle (4) with a pipette and the receptacle affixed to the glass body (2) with a glass joint. Now if air is withdrawn at (3), the air to be examined is drawn in at E, flows downward inside (2) and is finely dispersed into the solution through the glass frit. The vessel (2) is so constructed that, even at a pumping rate of 2 liters per minute, none of the solution is splashed onto (3) and all of the ozone comes to reaction. This was checked with reaction vessels connected in series. Reaction starts to become incomplete below 3°C. In the winter season, therefore, the air is drawn in through a glass

tube one meter in length and surrounded by a heating coil with 20 watts and an insulation layer.

After the completion of reaction, the solution is next forced back into the lowered receptacle (4) by blowing into (3). The remaining solution is flushed into the receptacle by spurting about 3 cc. bidistilled water in at (3).

Now the sodium thiosulphate content of the solution must be determined and compared with that of 3 cc of the reservoir solution. The difference is the equivalent of the iodine formed in the solution through the ozone which was drawn in.

If this difference is J γ iodine equivalent and if N liters of air were drawn through the solution, then the ozone content of the air is

$$O_3 = \frac{J [\gamma \text{iodine}] \cdot 1000 \left[\frac{\text{liter}}{\text{m}^3} \right]}{N [\text{liter}] \cdot 5.25 \left[\frac{\gamma \text{iodine}}{\gamma O_3} \right]} \quad J = \frac{1.93}{N} \left[\frac{\gamma O_3}{\text{m}^3} \right]$$

The most significant advance has been made by developing an iodine meter with which iodine in KI-solution, as well as sodium thiosulphate in KI-solution, can be measured with very great accuracy and sensitivity. This shall be described here briefly (?).

If two platinum electrodes are immersed in a potassium iodide solution and a potential which is less than the decomposition voltage is applied, so-called reversible iodine electrodes with a polarisation voltage equal to the applied potential are formed. Current drops to 0. But if free iodine (practically as I_2) is present in the solution, we obtain a current which, with very rapid movement of the solution against the electrodes, is proportional to the concentration of the free iodine in an extensive (six orders of magnitude) area. The solution is not changed through this measuring process. In our working model, a gramophone motor with an rpm control turns a holder into which the glass receptacles can be placed after being removed from the reaction vessel. We immerse the electrodes in the revolving glass near the moving sides and apply a voltage of 0.18 volt. First there results a polarisation current which quickly drops to a very small value, however, if excess sodium thiosulphate is present in the solution.

If iodine is now added, nothing changes until all the sodium thiosulphate is consumed, which of course the added iodine immediately transforms into sodium tetrathionate. The amount of iodine which is added above the original amount of sodium thiosulphate equivalent creates an increase in the iodine concentration proportional to the excess amount and we obtain a current

which is also proportional thereto.

Free iodine is not added chemically, but rather we produce it through electrolysis with a second pair of electrodes.

The wiring of the arrangement is shown in Illustration 10. The electrolytic current can be read at instrument J and adjusted with the resistors. According to Faraday's law, 1% of iodine is precipitated in 20 seconds at 38 μ A.

Illustration 11 shows the measurement current over electrodes 1 and 2 as a function of the time after connection for various electrolytic currents, but always with the same quantity of reserve solution and therefore with the same sodium thiosulphate content. It is seen that the current is initially not strong, but then becomes decidedly linear so that the point of intersection of these rising lines with zero current is very well defined. This, in addition to increased sensitivity, is the important advantage over titration with color change. The shaded breaking point of the curves are caused by the fact that, in practice, the solution cannot be ideally mixed at all times. The iodine is produced at the anode and must first be mixed with the solution. The smaller the electrolytic current, the sharper is the breaking point, but the longer the measurement.

Computation of the various bases yields the same quantity of iodine each time. Pictured here are calibrated measurements of a particular device which was designed for rapid measurement with an accuracy of 1/10 % iodine. It could also be set up for an accuracy of 1/1000 % iodine. (Notes the excessive numbers of instruments and the amount of time for a measurement would be much greater than, however).

Diluting the solution with water or a different temperature or a slower stirring or an ammeter G as in Illustration 10 with different standard constants have the effect only of changing the steepness of the rising lines in the current-time diagram. The base which determines the result is not influenced by these changes, however. This provides a great simplification of the measurement. Each individual measurement is completed in 3 to 4 minutes and can be documented automatically by a registering instrument. Flushing the electrodes and taking the readings requires less than half a minute if the electrolytic current was so selected that a simple numerical ratio exists between the basic unit of the time-scale and the quantity sought.

The sensitivity of the iodine meter makes it possible to carry out the ozone measurement with less than 1 liter of air. The air to be tested is drawn in with a membrane pump which shuts off automatically after a set number of revolutions. In addition, a never model activates, at the moment it shuts off, a valve which

switches the pump to a second washing tube. At the present time we are using 12 washing tubes each in Weissenau and Tübingen. A timer starts a measurement every two hours, each lasting 5 minutes.

Thus the twelve solutions need be replaced and evaluated only once each day. This can be easily accomplished by one person in one hour. If the solutions are protected from light, no error is incurred, all the more so because an additional receptacle is kept with the washing tubes with the same solution which then serves as the control element during evaluation.

The elimination of standard solutions is of great advantage in practice. The reliability of the measuring process results from the fact that if there is no ozone present the value 0 is indicated and the fact that multiple measurements carried out at the same time and place will yield results varying at most by 3%. This dispersion is mainly due to errors in pumping an exact volume of air. In practice, the greatest uncertainty is in the conversion of the pumped volume to air volume, especially if the air must be pre-heated. In view of the fluctuations of ozone content, these small instrumental errors are of no importance.

In our area, disturbances are caused only when smoke or industrial gases contaminate the monitoring site. The solution must then be buffered ($1 \text{ cc } 1/10(\text{Na}_2\text{HPO}_4 + \text{NaH}_2\text{PO}_4)$). Near the ocean an influence of Cl_2 can be expected which must be isolated by special measures. The buffer does not affect the ozone measurement of the electrolysis of the K^+ . According to our laboratory experiments, nitric oxides do not oxidize the neutral KJ . Under natural conditions, we were not able to find them in measurable quantities.

For very exact absolute measurements of ozone values, there are additional reaction possibilities between KJ and O_3 which should be considered. Studies are in progress on this subject. Their influence seems to be small on neutral solutions, however. Our method has the advantage that very little of the added quantity of KJ is consumed in the reaction and the hydrogen-ion concentration (pH) remains practically constant.

3. SUMMARY

The local ozone concentration of atmospheric air was measured regularly over a long period of time at several stations with an easily operated chemical measuring process. Some typical examples are shown, from which the destruction of ozone in the ground layer and the dominating influence of air exchange with higher layers can be clearly recognized. The method of measurement is briefly described.

4. References

(1) R. Auer, Gerlands Beiträge zur Geophysik (Gerland's Contributions to Geophysics), 1939, Vol 54, page 137. (2) E. Regener, Forschungs- und Erfahrungsberichte des Reichswetterdienstes (Research and Experience Reports of the Imperial Weather Service) A (No 9), 1941; Meteorologische Zeitschrift (Journal of Meteorology), 1943, Vol 60, page 253. (3) A. Ehmert and E. Ehmert, Forschungs- und Erfahrungsberichte des Reichswetterdienstes (Research and Experience Reports of the Imperial Weather Service) A (No 13), 1941. (4) A. Ehmert, *ibid.* (5) A. Ehmert, Report at the Special Convention "Ozone" of the Imperial Weather Service on 17 and 18 April 1944. (6) A. Ehmert, Meteorologische Rundschau (Meteorological Review), 1951, Vol 4, pages 64-68. (7) Cf. A. Ehmert, Zeitschrift für Naturforschung (Journal of Natural Research), 1949, Vol 4b, pages 324-327.

Note: (2), (3), (4) and (5) reprinted in Berichte des Deutschen Wetterdienstes, US Zone (Reports of the German Weather Service, US Zone), Nr 11, 1949.

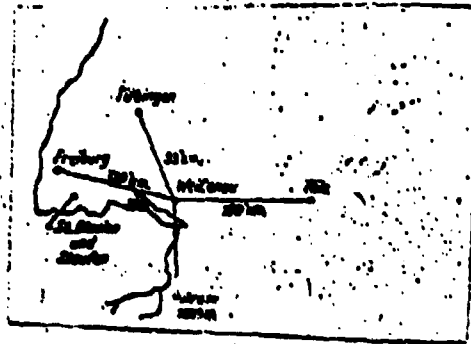


Illustration 1.

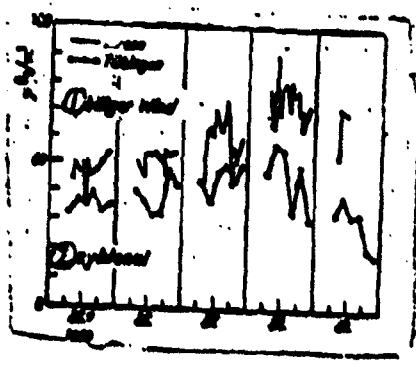


Illustration 2.

Legend: ① gusty winds
② cyclonic

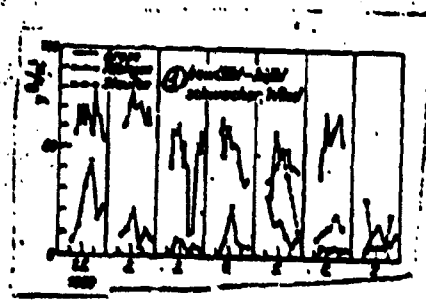


Illustration 3.

Legend: ① cool and overcast, weak winds

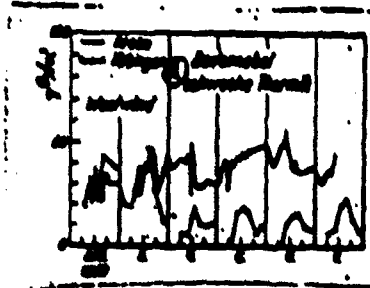


Illustration 4.

Legend: ① ground fog, weak thermic currents

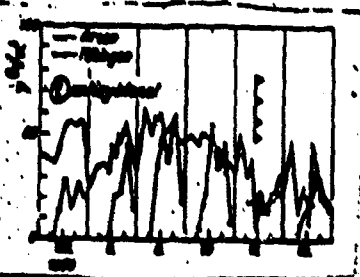


Illustration 5.

Legend: ① anti-cyclonic

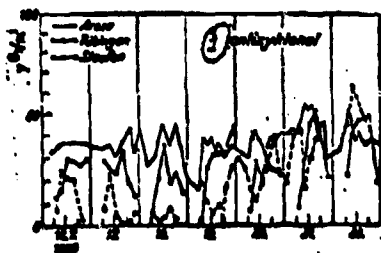


Illustration 6.

Legend: ① anti-cyclonic

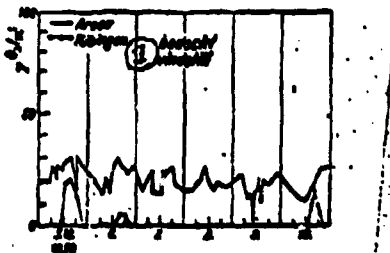


Illustration 7.

Legend: ① cloudy, calm

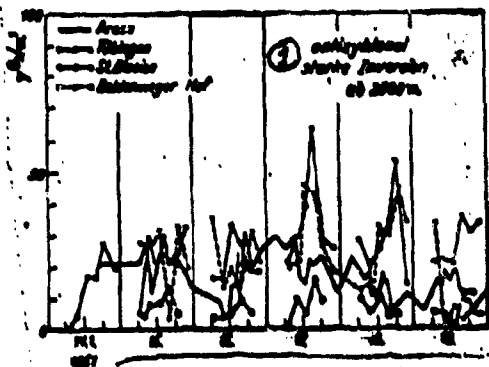


Illustration 8.

Legend: ① anti-cyclonic, pronounced inversion at 2000 meters

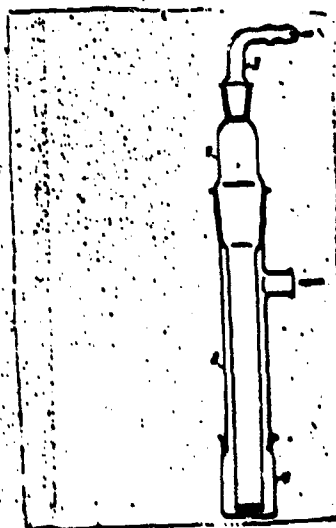


Illustration 9.

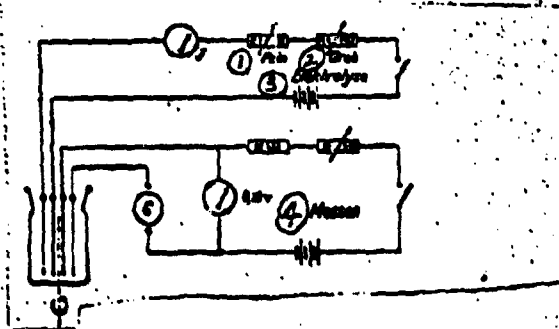


Illustration 10. Iodine meter.

- Legend: ① fine adjustment
 ② coarse adjustment
 ③ electrolysis
 ④ measuring

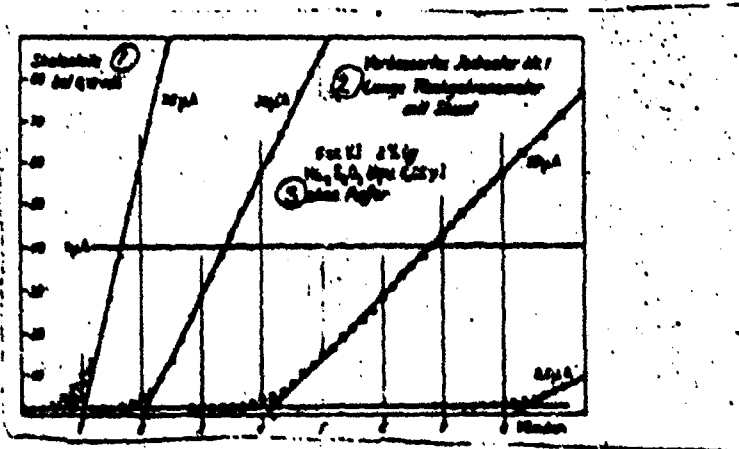


Illustration 11.

- Legend: 1) scale graduations at 0.10 volt
 2) improved iodine meter No 1
 long table galvanometer with shunt
 3) without buffer