

IO AND BrO IDENTIFICATION AT THE DEAD SEA

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INTRODUCTION

During the last decade, the importance of iodine oxide (IO) for tropospheric ozone destruction has been established in atmospheric chemistry. A previous study of bromine oxide performed at the Dead Sea showed frequent ozone depletion episodes down to mixing ratio of ozone less than 5 ppb. These ozone destruction episodes were always accompanied with high BrO levels up to above 150ppt. The study also revealed a diurnal repeating cycle of O₃ and BrO variation correlating with the solar radiation and wind direction [1], [2].

Spectroscopic measurements in an attempt to detect iodine oxide at the Dead Sea were performed for the first time in July-August 2001. IO mixing ratios above the detection limits were found on nearly every day of this campaign [3]. The maximum IO concentration reached levels above 12 ppt. Further a negative correlation of IO with BrO was observed. The present investigation was performed in order to substantiate the previous study and to also investigate the interaction iodine radicals with other species.

EXPERIMENTAL

The Dead Sea is a unique location, situated at the lowest point of the Earth's surface, it lies 415 m below the sea level. The Dead Sea is situated between N31°00 and N31°50' E035°30', and its dimensions are about 75 km long (in the north-south direction) and 15 km wide. It is one of the most saline lakes in the world with 5.6 g bromide l⁻¹ and 225 g chloride l⁻¹.

An investigation of bromine and iodine oxide was performed during field measurements in July 2003 at the Dead Sea. The instrumental equipment for these measurements included two independent differential optical absorption spectroscopy systems (DOAS) set up at Ein Bokek, 31°11'59N and 35°22'02E. The light path for both instruments was orientated in the north to south direction and was about 30m above the Dead Sea water level. For the IO measurement the light path distance was 8.6 Km (twice the distance between measuring site and retro-reflectors). The BrO measurements used a one-path instrument with a total light path of 3.7 km. The measurement period lasted from 1 July till 16 July 2003.

RESULTS

Bromine oxide detection and concentration values were calculated from recorded spectra. In order to obtain BrO data it was first necessary to correct to divide the measured spectra by the Fraunhofer structure observed from scattered sunlight in the relevant spectral region (304-364 nm). The evaluation and fitting procedure for BrO-spectra have been previously described

[2]. The BrO reference spectrum was calculated from the literature absorption cross section, NO₂ and O₃ spectra used in the calculations were obtained from actual measurements and calibrated against a literature absorption cross section. The absorption lines used in the fitting procedure to qualitatively and quantitatively identify for BrO were the 333.5 nm and 338.3 nm lines.

While iodine oxide was could clearly be identified in the obtained atmospheric spectra, the evaluation procedure for the IO was significantly more complicated than for BrO. This is due a number of reasons: the strong influence of the lamp light source on the measured spectra, the low IO concentration present (5-10 ppt), and the relatively high instrumental noise level. The following evaluation procedure was therefore employed to evaluate the spectra and included the following steps:

1. Subtraction of the offset and dark current spectrum from the air and background spectrum.
2. Followed by subtraction of the background air spectrum.
3. Band-pass filtration (high pass: division by the polynomial of the fifth order; low pass: 5 times adjacent smoothing).
4. Shift the spectrum to correlate with the lamp spectrum
5. Fit the measured spectrum to the lamp spectra and NO₂ reference spectra.
6. Fit the residual of the preceding operation to the IO reference spectra.

Figure 1 shows the IO reference spectrum and three measured spectra (4 July at 18:35; 5 July at 19:30; 6 July at 05:04) in the spectral 422-44 nm ranges. Two characteristic absorption lines (427.6 nm and 436.4 nm) are clearly visible in all of the resolved spectra. These lines were used for the IO-identification by DOAS measurements and its quantification using the fitting procedure. The IO reference spectrum was calculated from a literature absorption cross section. The concentration of IO spectra shown in figure 1, was calculated as $(9-10.5) \pm 1.5$ ppt with a detection limit of 2 ppt.

The IO values recorded for the periods of 2-6 July and 10-16 July are shown in figure 2. IO was observed, above the detection limit, on almost every day during these periods. The maximum IO concentration recorded was 10.5 ± 1.7 ppt reached on 4 July at 18:30 local summer time (LST=UT+3). The detection limits were relatively constant during the entire measurement period, 1.5-2.0 ppt. Negative mixing ratios on the figure 2 are due to statistical effects in the fitting routine. The maximum level recorded in the present study, 10.5 ppt, was almost identical to the maximum mixing ratio of 10.2 ppt observed in previous study at the Dead Sea performed in 2001 [3].

DISCUSSION

An examination of the figure 2 shows that the IO concentrations increase in the afternoon between 13:00-15:00 (LST) and reaches the first maximum before sunset (18:00-19:00 LST). After sunset, there is a slow decrease in the IO-concentrations and another increase takes place in early morning at sunrise. Figure 3 illustrates the diurnal variations in IO concentrations during the entire measurement period (02-06 July, 11-13 July, 14-16 July). It is evident from figure 3 that this pattern of concentration variations is typical for all the days, although it was more pronounced on July 5-6.

As observed in figure 4, elevated IO levels of up to 10.5 ppt were observed in the afternoons between 13:30 and 19:30 LST, with a maximum level reached around 19:40 LST. After sunset, a decrease in the IO concentration levels was observed decreasing to 4 ppt at 03:00 LST. A second increase in IO occurs in the morning at 05:00 LST reaching a level of 9.1 ppt. This was followed at 08:00 LST, by a strong decrease in IO to below the detection limit. It should be emphasized that during the entire measurement period, IO was never detected in the morning period, between 08:00 – 13:00 LST.

Figure 4 shows the diurnal variation for both IO and BrO during 5 days of the campaign (July 10,11,14,15,16) when simultaneous measurements were available for both parameters. As is observed, the two reactive halogen species show distinct different patterns. Comparison of the two parameters as shown in figure 5 indicates an anti-correlation trend between IO and BrO.

CONCLUSIONS

The present investigation has confirmed that IO is present in the atmosphere over the Dead Sea at concentrations of up to 10 ppt. The IO was observed to have a distinct diurnal pattern with IO peaking at two different periods: after sunset around 19:00 (LST) and just before sunrise, at 05:00 (LST). An anti-correlation was observed to exist between IO and BrO.

REFERENCES

- [1] Hebestreit, K., J. Stutz, D. Rosen, V. Matveev, M. Peleg, M. Luria, and U. Platt, DOAS Measurements of Tropospheric Bromine Oxide in Mid-Latitudes, *Science* 283, 55-57, 1999.
- [2] Matveev, V., M. Peleg, D. Rosen, D. Alper Siman-Tov, J. Stutz, K. Hebestreit, U. Platt, D. Blake, M. Luria, Bromine oxide – ozone interaction over the Dead Sea, *Journal of Geophysical Research* 106, 10375-10387, 2001.
- [3] Zingler, J., U. Platt, Spectroscopic measurement of iodine oxide at the Dead Sea, submitted *Journal of Geophysical Research* 2004.

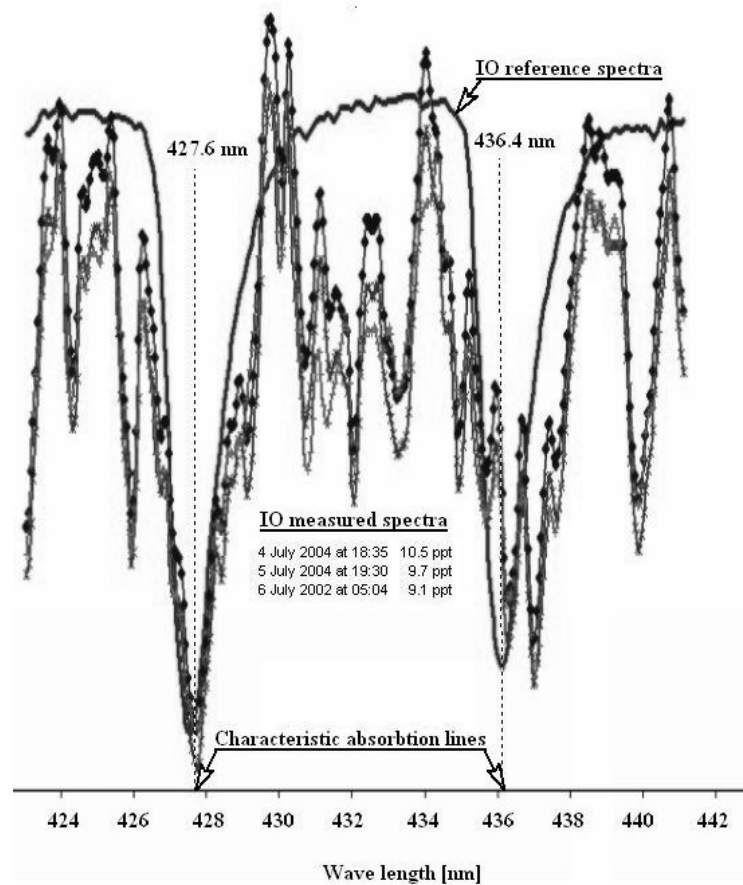


Figure 1: IO reference spectrum and three measured spectra

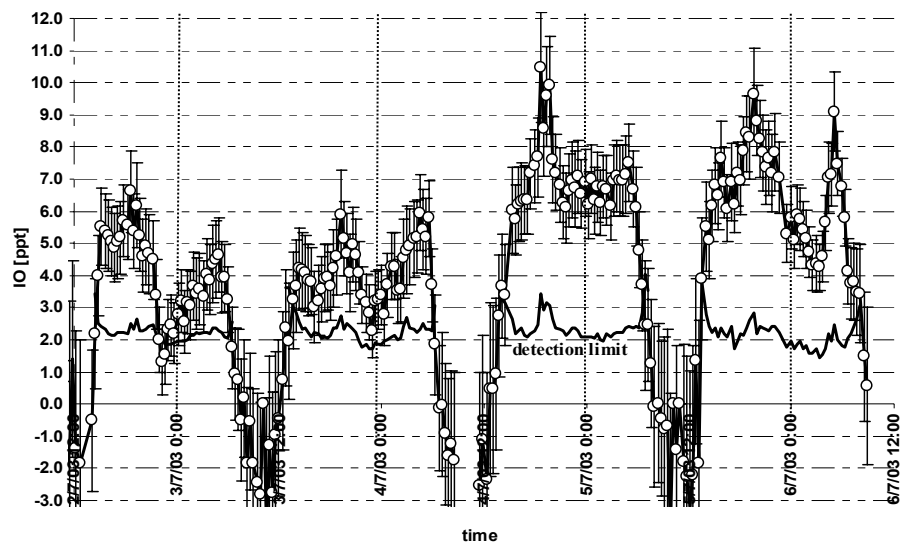


Figure 2a: IO concentration levels measured during 2-6 July 2003

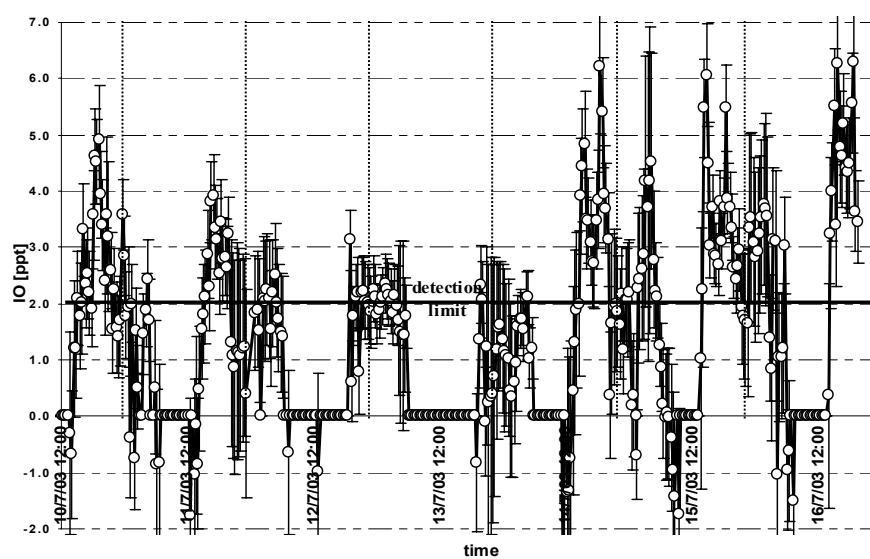


Figure 2: IO concentration levels measured during 10-16 July 2003

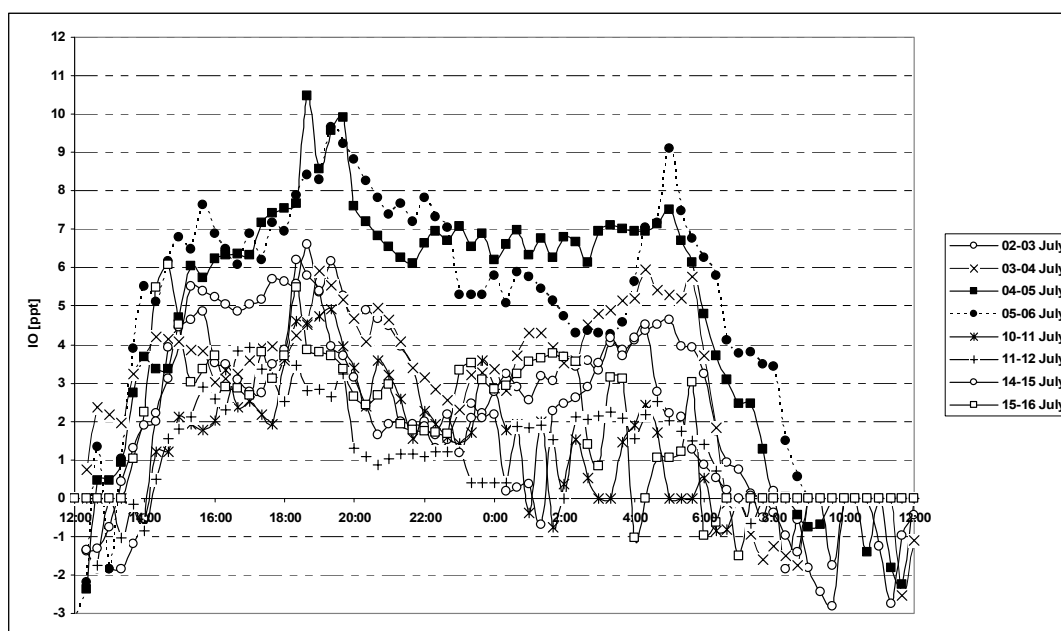


Figure.3: Diurnal variation in the IO-concentration

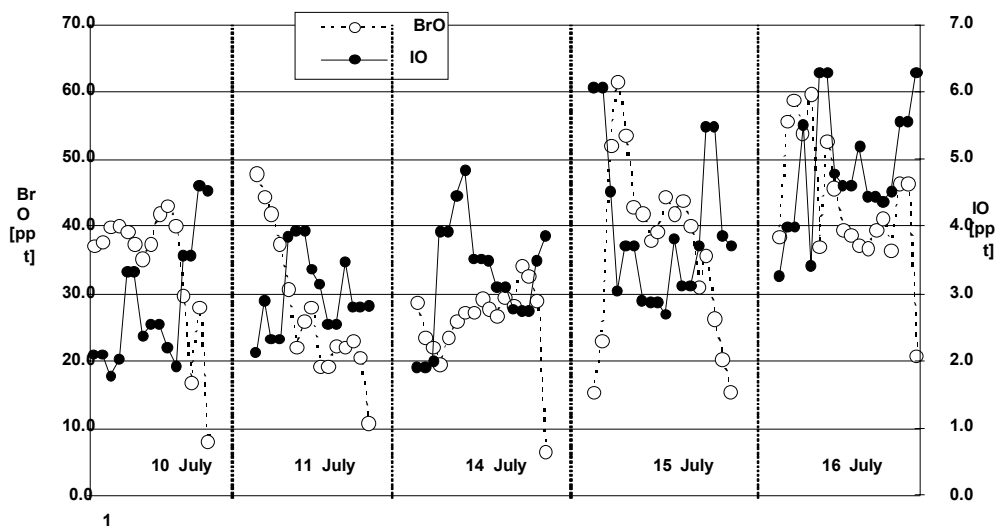


Figure 4: IO and BrO levels measured during 10-16 July 2003

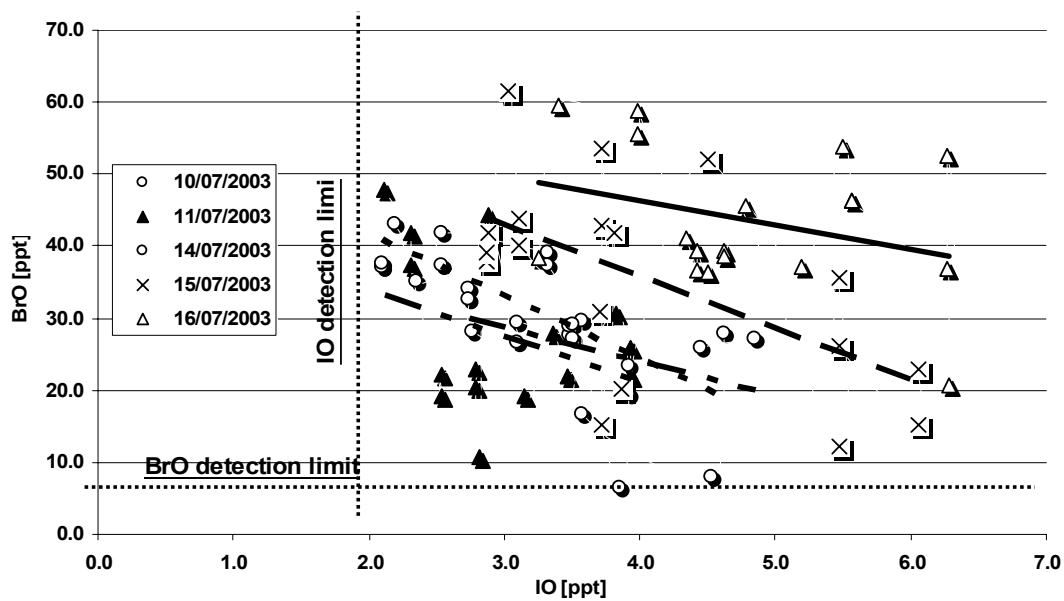


Figure 5: Correlation between IO and BrO