

ECC Ozonesondes response under controlled conditions

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Abstract

The ozone vertical profiles are recorded using ozonesondes coupled to aerological sondes in many stations around the world. If the surface ozone partial pressure ranges from 1-7 mPa, in the upper atmosphere minima below 1mPa in the troposphere and maxima above 25 mPa in the stratosphere are measured at mid-latitude stations.

The procedure for preparing and characterising the ozonesondes are more or less standard but a few questions are still unsolved regarding the sondes response in laboratory conditions and during the flights in real atmosphere. In particular, the question of the optimal KI-concentration used in the Electrochemical Concentration Cell (ECC) ozonesondes is important because there is no uniformity in the global network regarding this essential parameter. The stability of the response of the sondes is also difficult to characterise during the flight and therefore laboratory experiments are necessary. Time dependant response of the sondes may suggest memory effects which have to be also studied.

To help addressing some of these questions, MeteoSwiss has developed an automated calibration workbench that allows systematic measurements of the sondes characteristics in controlled laboratory experiments. The results of the analysis of recent tests carried out at MeteoSwiss will be presented and discussed in this contribution.

Introduction

Ozone sounding technique was developed in the sixties and a few operational ozone sounding stations have records as long as 40 years. This period covers the decline of the ozone layer which started around 1970 and also the development of the satellites technology. Therefore the ozone sounding datasets have a great value for trend assessment and for validation of satellites instruments.

However, one mPa of ozone corresponds to a current developed by the ECC ozonesondes cell of the order of 250 nA. Moreover, a high variation of the ozone with altitude is observed especially in spring with gradient as large as 0.04 mPa / m corresponding to 0.2 mPa / s for a 5 m/s ascent speed. It is therefore necessary to measure the current with ~10 nA resolution to see the details of such structures in the ozone profiles.

As shown in fig. 1, the ozonesondes consist mainly in a small pump and a reaction cell which contain a chemical solution. The oxidation of ozone molecules develops a current at the electrodes leads which is converted into ozone partial pressure (mPa) using the pump flow and pump temperature.

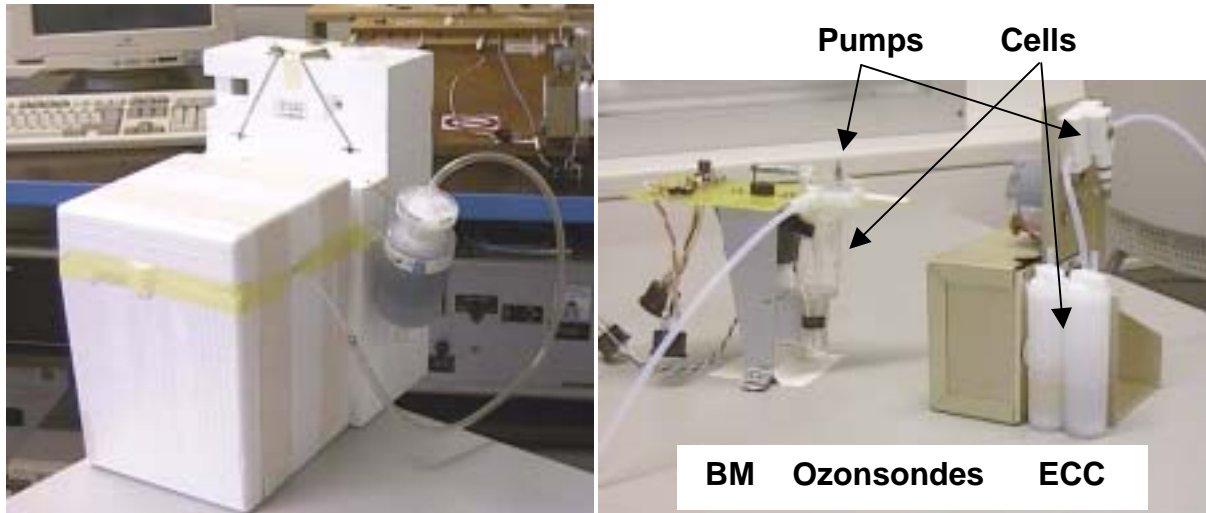


Figure 1: Left: Aerological sonde (PTU) box and the ozonesonde box attached together ready for launch. Right: the Brewer-Mast (BM) and Electrochemical Concentration Cell (ECC) ozonesondes.

Presently, a very large fraction of the ozone sounding stations use the ECC sondes but even after a long history of ozonesondings, there are still open questions about this measurement technique:

- What is the optimal solution strength (e.g. KI concentration, amount of buffer, etc.) ?
- What are the optimal preparation procedures for the ECC sondes ?
- What is the real response of the sondes to ozone change ?
- How the low pressure (high altitude) affects the pumps performances ?

MeteoSwiss is active in the field of ozone soundings technique and a unique workbench has been developed for ozonesondes preparation. If the primary role of the workbench is to assist the sounding team in the operational service for ozonesondes preparation, it allows also addressing the items listed above by designing specific laboratory experiments.

MeteoSwiss calibration workbench

In fig. 2, the standard equipment supplied by the manufacturers for the ECC sondes preparation is shown on the left and a MeteoSwiss workbench is presented on the right.



Figure 2: Left: Standard units for ECC ozonesonde preparation prior to the flight. Right: Laboratory equipment developed at MeteoSwiss for the preparation and testing of ozonesonde.

The standard unit (fig. 2 left) allows following the standard preparation cycle which consists in running the sondes under purified air for 10 minutes followed by an ozone flow of ~18 mPa for another 10 minutes and again pure air for 10 minutes. The usual sondes response parameters considered are:

- the back-ground current before (ib1) and after (ib2) the ozone flow measured at the end of the 10 minutes purified air sequences,
- the response time when the ozone is shut off,
- the pump current.

Besides these characteristics measured by the preparation unit, the pump flow is commonly measured in the laboratory by measuring the elapse time for a soap bubble to cover a calibrated glass tube.

In the MeteoSwiss workbench (fig. 2 right), the same preparation cycle is applied but the sequences are completely automated and digitally recorded. After the installation of the sondes on the workbench and the change of sensing solution, the operator doesn't intervene until the end of the preparation cycle. Moreover, the ozone measurements of the sondes are continuously compared to simultaneous measurements from a reference UV-photometer. The pump flow rate is measured with a mass flow meter. The advantages of the MeteoSwiss workbench are:

- a very good reproducibility of the operational service even if ten different operators are preparing the ozonesondes,
- a record of the sondes preparation since all important parameters are recorded in digital form,
- a great flexibility allowing programming different tests or repeating existing tests with strictly the same sequence of operations.

Different experiments have already been performed on this workbench and will continue in the future. In the following paragraphs, the results of some tests are reported.

Long term stability of the ozonesondes

In the course of the workbench development, a pair of recycled ECC sondes (ENSCI-0.5%) was used to run about 30 preparation cycles over a few days period.

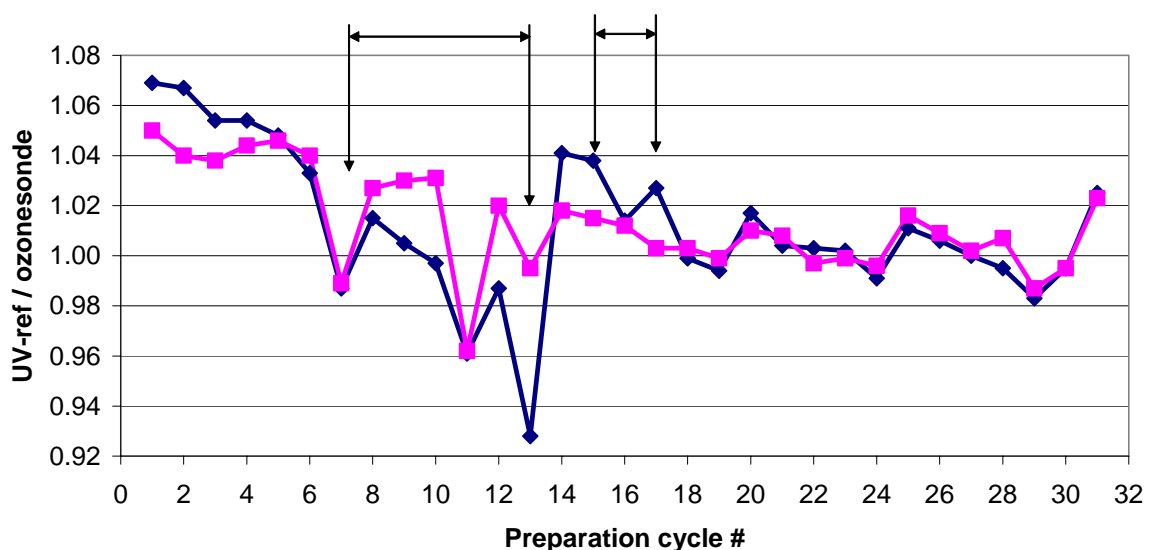


Figure 3: ECC ozonesonde responses (UV ref / ECC) after 31 preparation cycles. The arrows indicate preparation cycles without solution change and refill.

In fig. 3, the high ozone responses of both sondes are reported as the ratio “UV-ref / sonde”. It appears that the sondes have to be trained many times before the response actually stabilises to a ratio close to unity. The final variations are within +/- 2% compared to the reference UV-photometer. As a variant of the normal procedure, it was decided between sequences 8 - 13 as well as 15 - 18 to keep the same solution in the sondes cells to simulate flights times of respectively 4 and 2 hours. The effect of the evaporation of the solution is a decrease the electrodes surface immersed in the cathode solution and an increase the KI concentration. These double effects are noticeable at the preparation 13 for at least the sonde which had only about 0.8 ccm left of solution compared to the standard 3 ccm. In fig 4, the back-ground current measured at the end of the preparation cycles are reported. For this parameter also, there is a quite long stabilizing process that is present. The change of solution is also beneficial to attain a low residual current which is of the order of 20 +/- 10 nA for these sondes. This corresponds to less then 0.1 mPa of residual ozone signal.

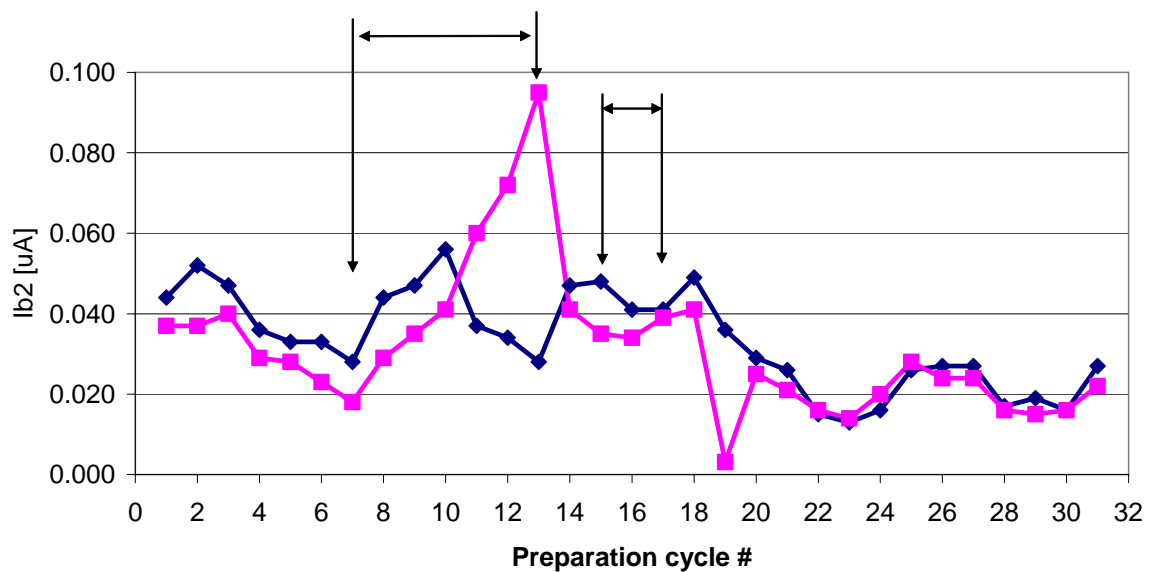


Figure 4: ECC ozonesonde back-ground signal after 31 preparation cycles. The arrows indicate preparation cycles without solution change and refill.

KI-concentration sensitivity for diluted solutions

The second experiment has been a study of the sensitivity of the ozonesondes response to the KI concentration in the chemical sensing solution. Presently in the global network different solutions are in use and the real effects of these differences are still not completely characterised. For this study, a 2% KI buffered solution has been prepared and from subsequent dilutions with water, solutions of 1.5%, 1.0%, 0.5% and 0.1% KI-concentration have been obtained. Five sondes have been filled up with a specific solution and tested 8 times repeatedly on the workbench over a six month period. After that, they have been launched the same day in five dual flights each with an operational sonde as reference. The laboratory results are presented in figs. 5 and 6 similarly to figs. 3 and 4. The KI concentrations effect is clearly visible and a systematic increase of the response with the concentration is present on both figures.

For the long term variation, the high ozone responses tend to increase between the first and five preparation cycles followed by a stabilisation. It is interesting to note the overestimation of the 2% solution and the net underestimation of the 0.1% solution. In the laboratory, the 0.5% solution is the closest to the UV-photometer reference. The same characteristics are apparent in fig. 6 with a 0.04 μA (0.1 – 0.15 mPa) back-ground current for the 2% solution gradually decreasing to 0 for the 0.5% solution. The 0.1% solution has a negative residual signal which shows an unconventional response with this much diluted solution.

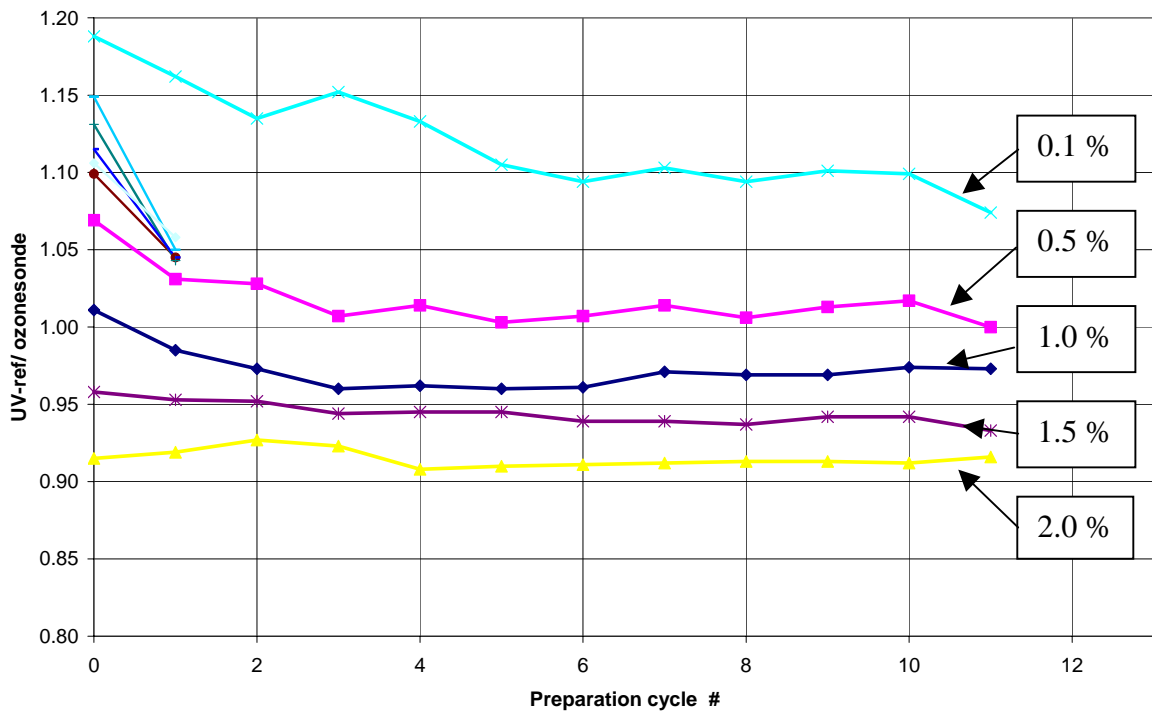


Figure 5: ECC ozonesonde responses (UV ref / ECC) after 11 preparation cycles of the KI concentration sensitivity experiment.

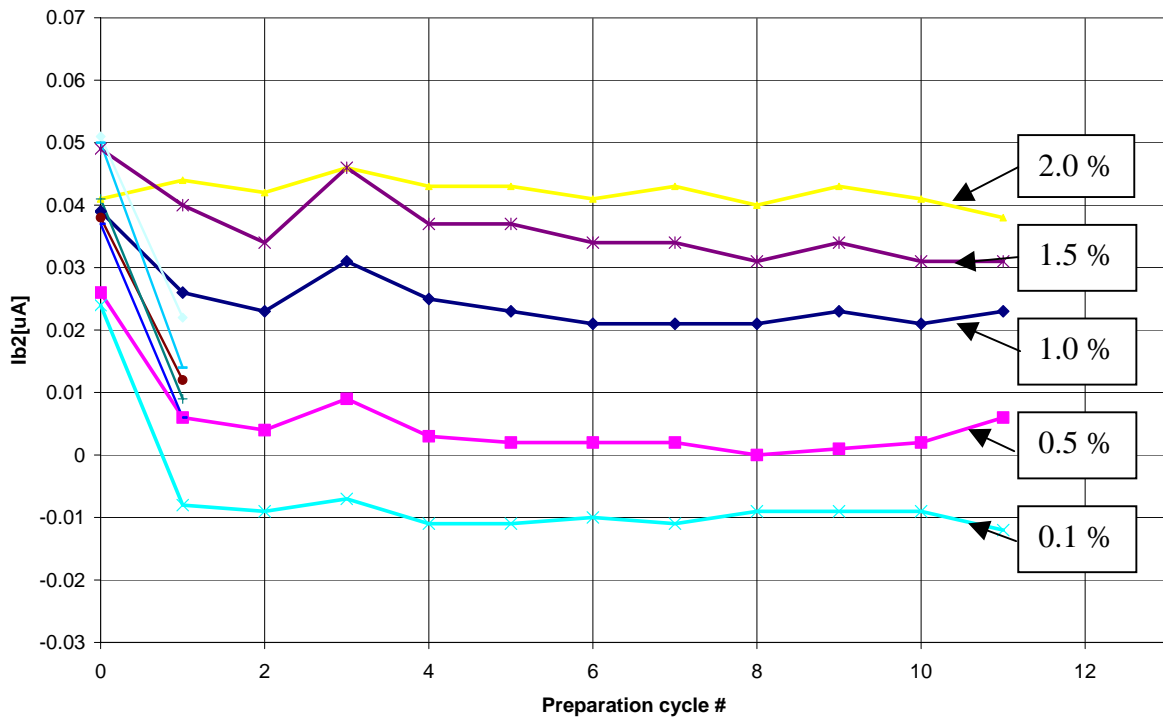


Figure 6: ECC ozonesonde back-ground current after 11 preparation cycles of the KI concentration sensitivity experiment.

Alternate solution composition

In the more recent experiment, tests are in progress by changing the balances of the different ingredients entering the composition of the sensing solution. The standard recipe for this solution consists of KI, buffer and KBr in specific proportion. Since the exact roles of the buffer substances and of the KBr are not easy to anticipate, solutions with decreased buffer and KBr have been prepared. Starting with a standard 0.5% KI solution, three solutions with respectively 1/4, 1/16 and 0 buffer quantities have been prepared. Similarly, a set of 4 solutions with KBr amount reduced to 1/4 of its normal amount have been prepared. Height ECC ozonesondes have been filled up with these different solutions and tested on the workbench. In figs. 7 and 8, the results of seven preparation cycles are reported similarly to the previous experiments.

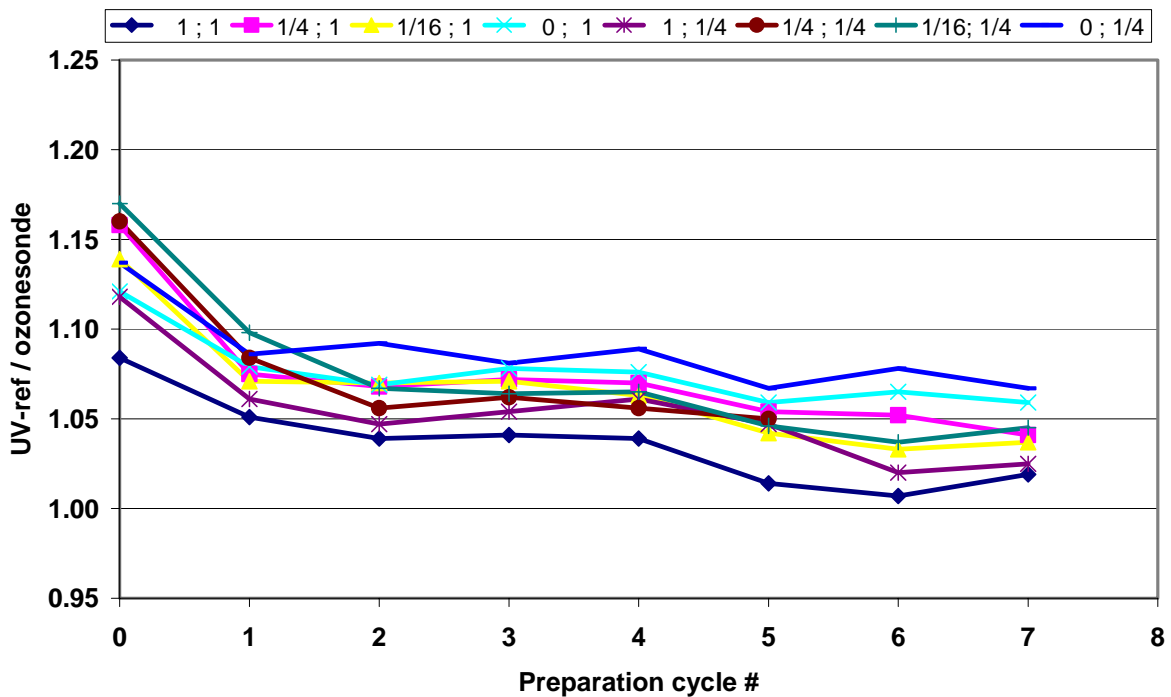


Figure 7: ECC ozonesonde responses (UV ref / ECC) after 7 preparation cycles of the solution composition experiment. The number given at the top refer to the relative amount of buffer, resp. KBr comparatively to the standard proportion.

As seen in fig. 7, the sequence of preparations does not show a systematic variation with the solution composition as clearly as for the previous experiments. After the fifth cycle, the standard solution (“1 ; 1”) and the solution with a reduced KBr (“1 ; 1/4”) are the closest to the reference UV-photometer. The largest difference is measured by the unbuffered and reduced KBr solution (“0 ; 1/4”) which tends to stabilise to a 7% difference.

Fig. 8 shows unusually large back-ground currents in the first cycle which have diminished with quite different rates: the fastest are characterised by lower buffer solutions and the slowest by the larger buffer solution. But this is more a tendency than a clear relationship. At that point, this experiment is still ongoing and further analyses of these data are still needed.

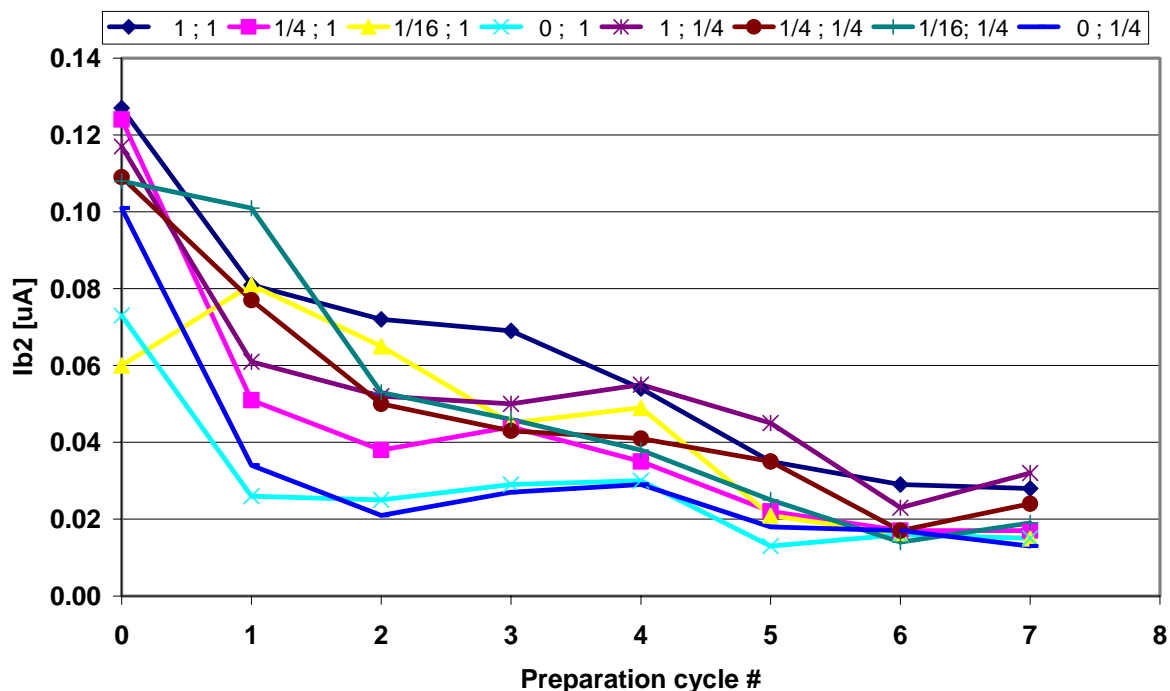


Figure 8: ECC ozonesonde back-ground current ib_2 after 7 preparation cycles of the solution composition experiment. The number given at the top refer to the relative amount of buffer, resp. KBr comparatively to the standard proportion.

Conclusion

In the following contribution, laboratory experiments on the behaviour of the ozonesondes have been presented. First the repetitions of the preparation cycles show some sort of aging or training effect of the ozonesondes response. In the concentration experiment, the sensitivity of the sondes response to the KI concentration is well marked for the residual signal as well as for the high ozone response. In the third experiment presented here, the effect of the solution composition is still under analysis and only qualitative conclusions are drawn at that stage.

Along the history of the ozone soundings, the preparation procedures and the sensing solutions composition has been changed many times. In general, the documentation of these changes is not easily accessible or even not existing in digital form. For example, the KI concentration has been gradually reduced from 2% to 0.5% in various stations. A quick look at fig. 5 allows expecting a trend in the data just connected to the concentration change. The present results are a signal that such changes have to be taken into account if possible when working with long ozone sounding series.