For more information, please contact:
World Meteorological Organization
Research Department
Atmospheric Research and Environment Branch
7 bis, avenue de la Paix – P.O. Box 2300 – CH 1211 Geneva 2 – Switzerland
Tel.: +41 (0) 22 730 81 11 – Fax: +41 (0) 22 730 81 81
E-mail: AREP-MAIL@wmo.int
Website: http://www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html

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GAW Report No. 201

Quality Assurance and Quality Control for Ozonesonde Measurements in GAW

GLOBAL ATMOSPHERE WATCH

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Chair, Publications Board
World Meteorological Organization (WMO)
7 bis, avenue de la Paix
P.O. Box 2300
CH-1211 Geneva 2, Switzerland

Tel.: +41 (0) 22 730 84 03
Fax: +41 (0) 22 730 80 40
E-mail: publications@wmo.int

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WORLD METEOROLOGICAL ORGANIZATION
GLOBAL ATMOSPHERE WATCH

Quality Assurance and Quality Control

for Ozonesonde Measurements in GAW

Prepared by Herman G.J. Smit
and the
Panel for the Assessment of Standard Operating Procedures for Ozonesondes (ASOPOS)

World
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WATCH

January 2013

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PREFACE

PREFACE

Ozone is a key trace gas in the atmosphere surrounding our planet: Ozone in the stratosphere absorbs the detrimental part of solar radiation, thus protecting life (in its present form) at the Earth's surface. The stratospheric ozone layer has been in danger due to manmade emissions of ozone depleting substances (ODSs, such as chlorofluorocarbons). Thanks to the actions taken by the Parties to the Montreal Protocol (1987, and subsequent amendments and adjustments) one expects the ozone layer to recover over the next several decades. Ozone in the air that we breathe is the key species of air pollution known in large metropolitan areas as photochemical smog, and ozone is the main species determining the oxidation capacity of the atmosphere, removing many compounds (including toxic substances) from tropospheric air. Last but not least, ozone in the tropopause region is a strong greenhouse gas. In order to investigate these important problems reliable field measurements are very important. One of the backbone elements of the Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) are measurements performed from relatively small and lightweight balloons (ozonesondes) that provide data on the vertical distribution of ozone, which is crucial information for the understanding the key role that ozone plays in the atmosphere.

Regular measurements with ozonesondes started in the second half of the 1960s at a few sites. Prof. Volker Mohnen was among the first to point out the crucial role of the data quality of ozonesondes, particularly when long-term changes need to be determined reliably. He supported the construction of the chamber facilities JOSIE (Juelich Ozonesonde Intercomparsion Experiment), allowing testing of ozonesondes in laboratory facilities simulating a wide range of atmospheric conditions. These tests clearly showed the need to standardize the measurements made with electrochemical concentration cell (ECC) ozone sensors, leading to the establishment of the expert panel ASOPOS (Assessment of Standard Operating Procedures for Ozonesondes). These activities were supported by AREP-WMO representatives, John Miller and Michael Proffitt. The JOSIE results were basically confirmed by the field campaign BESOS (Balloon Experiment on Standards for Ozonesondes) and by dual flight experiments. This information was the basis for standard operating procedures (SOPs) of ECC sondes, which were approved by the Scientific Advisory Group for Ozone at their annual meeting in 2007.

The scientific community contributing to ASOPOS includes representatives of different networks involved in long-term ozone monitoring, namely GAW, NDACC (Network for the Detection of Atmospheric Composition Change) and SHADOZ (Southern Hemisphere Additional Ozonesondes). On behalf of the GAW Programme of WMO, that supports atmospheric chemistry research, we are very pleased to introduce the ASOPOS report, which comprehensively summaries the adopted SOPs for ECC and other types of ozonesondes together with the required scientific knowledge including a comprehensive reference list. We hope that the community formed by ASOPOS will continue to coordinate the scientific research and the further development of this important ozone measurement system.

1. INTRODUCTION

Ozone, although a minor constituent, plays a key role in the physics and photochemistry of the atmosphere. As an important absorber of both infrared- and ultraviolet-radiation ozone is of crucial importance for Earth's climate but also as an UV-filter for the biosphere. Human activities can change the ozone distribution substantially through the emissions of gases like chlorofluorocarbons (CFCs), nitrogen oxides (NO_X), carbon monoxide (CO) and hydro carbons (CHs). This raises important questions about its environmental impact on our Earth system [e.g. *Intergovernmental Panel on Climate Change (IPPC),* 2001, 2007, *WMO-Scientific Assessment of Ozone Depletion,* 2002, 2006]: What is the effect of human activity on stratospheric and tropospheric ozone? How is the UV flux at the surface of the Earth changing in response to changes in the ozone column density? How is climate sensitive to the ozone and what factors control these concentrations? How is the oxidizing power of the atmosphere changing with time, and what is the influence of human activity? How is regional air quality degraded by industrial and other anthropogenic emissions in populated areas of the world? To answer these questions the Global Atmosphere Watch (GAW, http://www.wmo.ch/web/arep/gaw/gaw_home.html) programme as a coordinated network of observing stations, associated facilities and related scientific assessment activities supply basic information to be used by policy makers to resolve these important environmental issues [*Global Atmosphere Watch Guide, GAW Report No.86*, 1993].

As a major component in GAW the global network of ozone sounding stations (See Figure 1-1) provides the longest time series of the vertical ozone distribution between surface and 30-35 km altitude [GAWSIS, http://www.empa.ch/gaw/gawsis]. Up to an altitude of about 20 km ozonesondes constitute the most important data source with long term data coverage for the derivation of ozone trends with sufficient vertical resolution, particularly in the important, climate sensitive, altitude region around the tropopause [*SPARC-IOC-GAW Assessment of Trends in the Vertical Distribution of Ozone*: *1998*]. Furthermore, ozonesondes are widely used in field campaigns to study photochemical and dynamical processes in the atmosphere and to validate and evaluate satellite observations and their long term stability. Organized in strategic and well-designed ozone sounding networks such as South Hemispheric Additional OZonesondes (SHADOZ) in the tropics [e.g., *Thompson et al.,* 2003], IONS (INTEX Ozonesonde Network Study) in mid-latitudes [*Thompson et al.,* 2007] and MATCH in the polar regions [e.g. *von der Gathen,* 1995] ozonesondes can become a powerful research tool in atmospheric science [*Thompson et al.*, 2011].

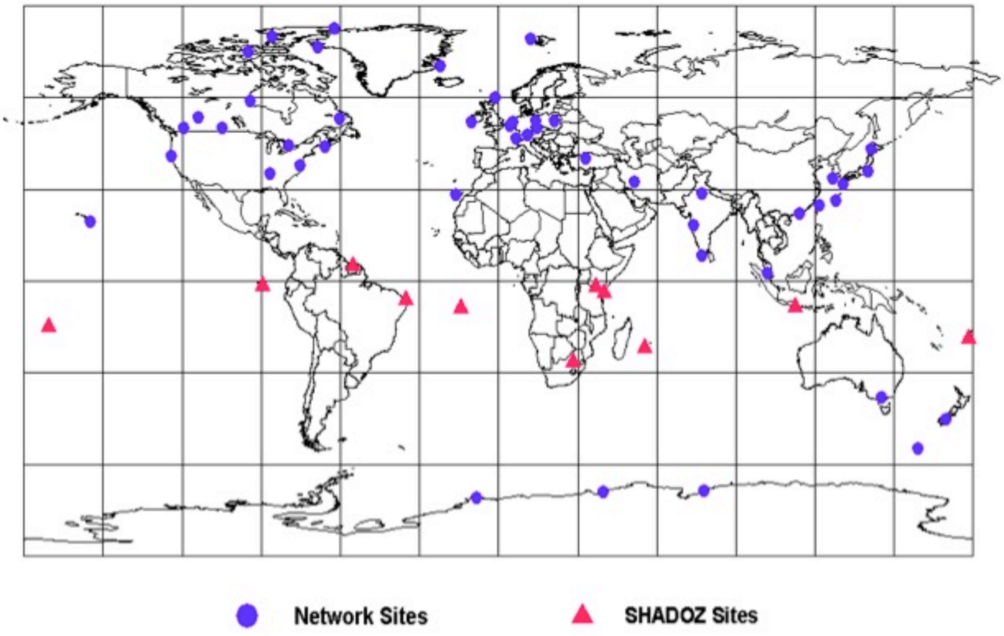

Figure 1-1: WMO/GAW-global network of ozone sounding stations. The red symbols represent sites of GAW-contributing partner SHADOZ

Ozonesondes are small, lightweight and compact balloon borne instruments, developed for measuring the vertical distribution of atmospheric ozone up to an altitude of about 30-35 km [e.g. *Smit*, 2002]. The sensing device is interfaced to a standard meteorological radiosonde for data transmission to the ground station and can be flown on a small rubber balloon (See Figure 1.2). Three major different types of ozonesondes, i.e. Brewer-Mast [*Brewer and Milford,* 1960], electrochemical concentration cell (ECC) after *Komhyr* [1969], and the carbon iodine cell [*Kobayashi and Toyama*, 1966], are in use. Each sonde type has its own specific design [e.g. *Smit*, 2002] but all the sensors utilize the principle of the fast reaction of ozone and iodide within an electrochemical cell.

**Figure 1-2: Ozonesondes launches on different sites of the Earth:
Top left - South Pole Station (By courtesy of NOAA Earth System Research Laboratory GMD); top right - Meteorological Observatory Hohenpeissenberg, Germany (By courtesy of German Weather Service, DWD); bottom left - Shipboard from RV "Ronald Brown" (Operated during INDOEX 1999 over Indian Ocean) and bottom right - SHADOZ-station Irene, South Africa, (Operated by South African Weather Service)**

Consistency of instruments with regard to their quality and characteristics is a pre-requisite to assure consistent sonde measurements [*SPARC-IOC-GAW Assessment of Trends in the Vertical Distribution of Ozone*, 1998]. Each ozone sounding is made with a new instrument, which has to be characterized prior to flight. Therefore, it is absolutely essential to have agreement on procedures for preparation as well as agreement on procedures for data processing and analysis. Ozonesondes have gone through several modifications since they were first manufactured, which adds uncertainty to trend analysis. Routine testing of newly manufactured ozonesondes will help to ensure confidence in observed trends in the future. Therefore, as part of the quality assurance (QA) for ozonesondes that are in routine use in the GAW the environmental simulation facility at the Research Centre Juelich (http://www.fz-juelich.de/iek/iek-8/EN/Expertise/Infrastructure/ESF/ESF_node.html) has been established as the World Calibration Centre for Ozonesondes (http://www.fz-juelich.de/iek/iek-8/EN/Expertise/Infrastructure/WCCOS/WCCOS_node.html) [*GAW-Report No. 104,* 1995] with following three major QA-tasks:

• QA-Procedures:	Establishment and up-date of Standard Operating Procedures (SOP's) of different sonde types
• QA-Manufacturers:	Performance check of sondes from different manufacturers
• QA-Operation:	Evaluation of sonde operating practice of sounding laboratories

The simulation facility enables control of pressure, temperature and ozone concentration and can simulate flight conditions of ozone soundings up to an altitude of 35 km, whereby a UV-photometer serves as a reference [*Smit et al*., 2000].

In the scope of this QA-plan for ozonesondes since 1996, JOSIE (= Juelich Ozonesonde Intercomparison Experiment) activities (http://www.fz-juelich.de/iek/iek-8/EN/Expertise/Infrastructure/JOSIE/JOSIE_node.html) have been conducted at the simulation facility to assess the performance of ozonesondes of different types and manufacturers [see *Smit and Kley*, 1998 (GAW Reports No. 130), *Smit and Straeter,* 2004a,b (GAW Reports No. 157, 158)]. In order to determine precision, accuracy and response of the ozonesondes as a function of sonde type, altitude, and ozone level, the different ozonesonde types were tested under a variety of conditions and compared with an accurate UV-photometer. Special attention was paid to outstanding issues with a strong focus on the influence of operating procedures on in-flight performance, particularly for the widely used ECC-sonde type [*Smit et al.,* 2007].

JOSIE demonstrated that the achievement of good precision and high accuracy is not only strongly dependent on sonde type but also particularly on handling [*Smit et al.,* 2007]. The intercomparisons showed that small differences in instrument construction or operating procedures can significantly influence the sonde performance. For example, the performance characteristics of two different ECC-sonde types, manufactured by either Science Pump Corporation (Model type: SPC-6A) or Environmental Science Corporation (Model type ENSCI-Z), can be significantly different, even when operated under the same conditions. Different ozone readings were obtained when sondes of the same type are operated with different cathode sensing solutions. This means that for ozone sounding stations performing long term measurements a change of the sensing solution type or ECC-sonde type can easily introduce a sudden step of ±5% or more in their records, affecting determination of ozone trends. In general JOSIE demonstrated that standardization of operating procedures for sondes is a pre-requisite that will yield the best precision and accuracy.

In order to achieve standardization of operating procedures WMO/GAW initiated in 2001 the Assessment of Standard Operating Procedures for OzoneSondes (ASOPOS). Major goal of ASOPOS is to establish a set of standard operating procedures (SOPs) that will be recommended and documented by the WMO for each of the three major types of ozonesondes (ECC, BM+hybrids and KC79/96) used in the GAW ozone sounding network. After a critical evaluation of the entire series of JOSIE-experiments preliminary SOP's (Standard Operating Procedures) were unanimously agreed upon by a panel of ozonesonde experts at Geneva, Switzerland in April 2001.
In April 2004, the WMO/BESOS (Balloon Experiment on Standards for Ozonesondes) field campaign at the University of Wyoming at Laramie, USA, was conducted to test the provisional SOP's for ECC-ozonesondes in the real atmosphere. The BESOS balloon gondola contained 18 ozonesondes, which were individually prepared according to the preliminary SOP's. For an in situ ozone reference the same UV-photometer, as used in JOSIE at WCCOS in Juelich, was included on the gondola. BESOS focused exclusively on the influence of the use of different sensing

solutions on the performance of ECC-sondes from the two different manufacturers [*Deshler et al.*, 2008].

In September 2004, a WMO/ASOPOS meeting of ozonesonde experts was held at Juelich, Germany to evaluate the BESOS-results in combination with the results from JOSIE- and other laboratory and field studies to finally establish WMO-recommended SOP's, for the different major types of ozonesondes used in the GAW-ozone sounding network. Unanimous agreement on SOP's was achieved by the ASOPOS-panel. Also it was concluded that the sonde to sonde differences observed in JOSIE are borne out in BESOS, such that the JOSIE-simulation chamber experiments are representative of the real atmosphere. Standardization of the operating procedures (SOP's) leads to the best precision.

The results of the JOSIE 1996-2000 experiments, their design and results are presented in detail in three GAW reports [*Smit and Kley,* 1996 and *Smit and Straeter*, 2004a & 2004b) and evaluated in peer reviewed literature by Smit et al. [2007]. The BESOS results are presented and evaluated by *Deshler et al.,* 2008. In addition, the SOP's for ECC-sondes were approved by the Science Advisory Group for ozone (SAG-O_3) of GAW at their annual meeting in at Tenerife in May 2007. One of the most crucial recommendation made by the ASOPOS panel was on the use of cathode sensing solution strength for the different ECC sonde types:

- SPC-6A: 1.0% KI, full buffer (SST1.0)
- ENSCI-Z: 0.5% KI, half buffer (SST0.5)

In order to avoid any misunderstanding:

At present only new ozone sounding stations should follow this recommendation on the use of sensing solution and ECC sonde type. Existing sounding stations should not change ECC sonde type or sensing solution type.

This report gives an overview of the different aspects of quality assurance and quality control for ozonesonde measurements in GAW. Chapter 2 describes the major types of ozonesondes operational in GAW-sounding network. Chapter 3 deals with the different aspects of data quality: (i) factors influencing the sonde performance (ii) review of the performance of the different sonde types in the stratosphere as well as in the troposphere. Chapter 4 provides an overview of the standard operating procedures (SOPs) for each of the three major ozonesonde types. With regard to SOP's for ECC-sonde types this will be done in the scope of ASOPOS and the major conclusions and recommendations given by the panel of ozonesonde experts. This includes also ASOPOS recommendations with respect to data archiving (e.g. data content and data format) and data submission to the World Ozone and UV Data Centre (WOUDC, http://www.woudc.org) at Toronto, Canada. Chapter 5 serves as a guide for users of ozonesonde data with respect to different qualifiers indicating the quality of the different sounding data records. In Annex-A, for each sonde type, a comprehensive step by step practical guide of how to operate ozonesondes is provided for launch site operators.

2. OZONESONDES

2.1 Introduction

Ozonesondes are small, lightweight and compact balloon borne instruments , developed for measuring the vertical distribution of atmospheric ozone up to an altitude of about 30-35 km. The set up of an ozone sounding system is shown in Figure 2-1. During normal flight operation, ozonesondes are coupled via special interfacing electronics with standard meteorological radiosondes [e.g. *Dabberdt et al.*, 2005] for data transmission of the measured sensor current and pump temperature plus additional measurements of aerological parameters like pressure, temperature, and humidity (optionally wind direction and speed[1]). Using the telemetry of the radiosonde the data measured by the sonde is transmitted to the ground station for further data processing.

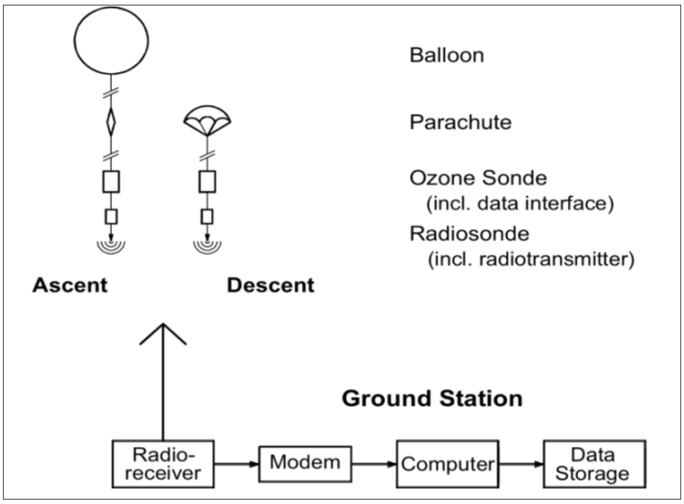

Figure 2-1: Set up of an ozone sounding system

Total weight of the flight package is typically about 1 kg and can be flown on small weather balloons (See Figure 2-1). Normally data are taken during ascent, at a rise rate of about 5 m/s, to a balloon burst altitude of 30-35 km. The inherent response time of the ozonesonde is 20-30s such that the effective height resolution of the measured vertical ozone profile is typically 100-150 m.

Figure 2-2 shows some examples of vertical ozone sounding profiles obtained at a mid-latitude site (Juelich, Germany), over the tropical Atlantic (RV “Polarstern) and at the Antarctic (South Pole), respectively. Ozonesondes can be flown under almost all weather conditions even under heavy clouds , rain, or snow where optical profiling techniques are limited under these conditions.

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[1] *The windfinding capabilities of modern type of radiosondes are based on the GPS (Global Positioning System) satellite navigation, while elder radiosonde types are using terrestrial radio navigation systems such as Loran-C or Omega [e.g. Dabberdt et al., 2005]*

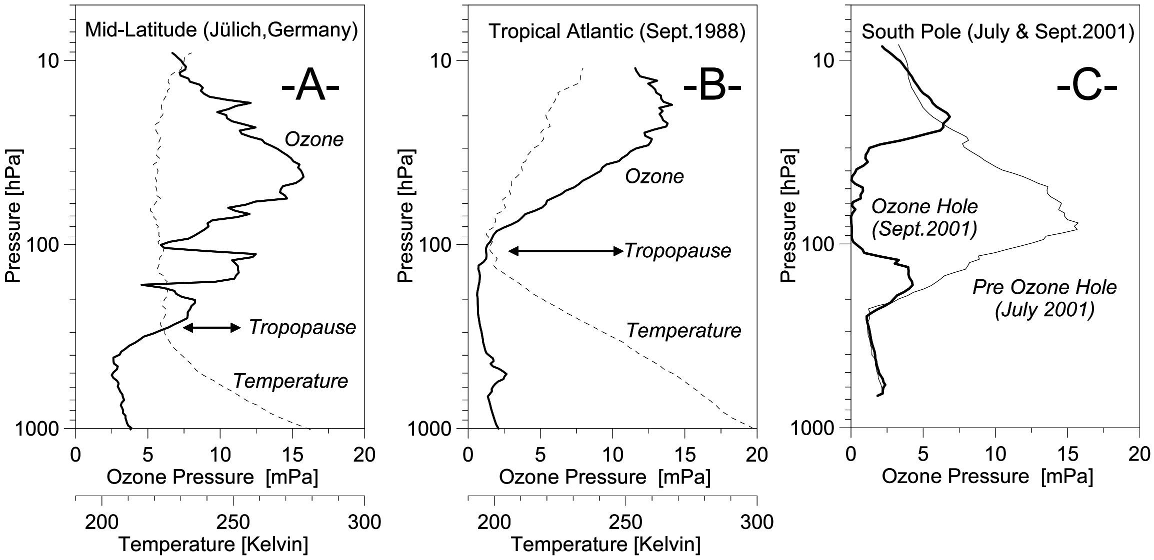

Figure 2-2: Vertical ozone sounding profiles. (A) mid latitude (Juelich, Germany, 51°N, 6°E, March 1994), (Provided by FZJ); (B) tropical Atlantic (RV "Polarstern", 6°N, 30°W, September 1988), (Provided by FZJ); (C) : South Pole (pre-ozone hole in July 2001 and ozone hole in September 2001, (Provided by NOAA/GMD)

2.2 Principle of Operation

The ozone measurement of the electrochemical sonde is based on the titration of ozone in a potassium iodide (KI) sensing solution according the redox reaction:

[R-2-1] $2\,KI + O_3 + H_2O \longrightarrow I_2 + O_2 + 2\,KOH$

The amount of generated „free" iodine (I_2) is measured in electrochemical reaction cell(s). Continuous operation is achieved by a small electrically driven gas sampling pump which bubbles ambient air through the sensing solution of the electrochemical cell. Transported by the stirring action of the air bubbles, the iodine makes contact with a platinum cathode and is reduced back to iodide ions by the uptake of 2 electrons per molecule of iodine.

[R-2-2] $I_2 + 2e \xrightarrow{Pt} 2\,I^-$ [cathode reaction]

An electrical current I_M [µA] generated in the external circuit of the electrochemical cell is, after correction for a background current I_B [µA], directly related to the uptake rate of ozone in the sensing solution. By knowing the gas volume flow rate Φ_P [$cm^3 s^{-1}$] of the air sampling pump, its temperature T_P [K] and the conversion efficiency of the ozone sensor η_C, the measured partial pressure of ozone P_{O3} [mPa] is determined by the relation:

[E-2-1] $$P_{O3} = 0.043085 \cdot \frac{T_P}{(\eta_C \cdot \Phi_P)} \cdot (I_M - I_B)$$

The constant 0.043085 is determined by the ratio of the gas constant, R, and the Faraday constant, F[2] divided by 2 (the number of electrons produced in the sensor cell per ozone molecule). The electrical cell current I_M and pump temperature T_P are measured in-situ during the

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[2] *The number of moles of ozone, n_{O3}, sampled per second and cm^3:* $n_{O3} = (I_M - I_B) / (\eta_C \cdot 2 \cdot F \cdot \Phi_P)$ *whereby F is Faraday's constant (= 9.6487×10^4 C $mole^{-1}$). By applying ideal gas law the corresponding partial pressure of ozone can be expressed as* $P_{O3} = \frac{R}{2F} \cdot \frac{T_P}{(\eta_C \cdot \Phi_P)} \cdot (I_M - I_B)$, *whereby R is universal gas constant (=8.314 J K^{-1} $mole^{-1}$).*

sounding. The background current I_B and volumetric flow rate Φ_P of the gas sampling pump of each sonde are measured in the laboratory at ambient air pressure during pre-flight preparations.

The conversion efficiency η_C is determined by the absorption efficiency of O_3 into the sensing solution and the stoichiometry of the conversion of O_3 into I_2. During normal operation the conversion efficiency η_C is about one at neutral pH [*Saltzman and Gilbert*, 1959]. Usually a sodium-hydrogen phosphate buffer is added to the cathode sensing KI-solution to keep the pH neutral at 7.0. Further, potassium bromide (KBr) is added as a supporting electrolyte and probably stabilizes the conversion of ozone into iodine [*Saltzman and Gilbert*, 1959]. Equation [E-2-1] is valid if no ozone is destroyed in the sampling system, each ozone molecule produces two Iodine molecules, and if there are no interfering reactions in the solution from minor constituents other than ozone in the air sample [*SPARC-IOC-GAW*, 1998].

2.3 Major Ozonesonde Types

Three major different types of ozonesondes, i.e. electrochemical concentration cell (ECC) after *Komhyr* [1969], Brewer-Mast (BM) [*Brewer and Milford,* 1960], and the carbon iodine cell (KC96) [*Kobayashi and Toyama*, 1966], are presently in use. Although the principle of operation is similar for all three sonde types, the instrumental layouts have significant differences and each sonde type has its unique design [e.g. *Smit*, 2002].

2.3.1 Electrochemical Concentration Cell Ozonesonde (ECC)

The ECC (=Electrochemical Concentration Cell) ozonesonde, developed by *Komhyr* (1969, 1971), is nowadays most widely used. More than 80% of the stations of the world wide WMO/GAW ozone sounding network uses ECC-sondes. The ECC-ozone sensor is an electrochemical cell consisting of two half cells, made of Teflon or molded plastic, which serve as cathode and anode chambers, respectively. Both half cells contain platinum mesh electrodes. They are immersed in a KI-solution of different concentrations. The two chambers are linked together by an ion bridge in order to provide an ion pathway and to prevent mixing of the cathode- and anode electrolytes.

The ECC sensors do not require an external electrical potential. This is in contrast to the Brewer-Milford type of electrochemical ozone sensor [*Brewer et al.,* 1960]. The ECC gets its driving electromagnetic force from the difference in the concentration of the KI-solution in the cathode- and anode chamber, 0.03-0.06 Mol/l (=0.5-1% KI) and ≈8.0 Mol/l (KI-saturated) respectively. A chemically inert gas sampling pump made of Teflon (Komhyr, 1967) bubbles ozone in ambient air through the cathode cell with the lower concentrated KI-sensing solution and causes an increase of"free“ iodine (I_2) according the redox reaction [R-2-1]. At the surface of the Pt-cathode, I_2 will be converted to I^- through the uptake of two electrons [R-2-2], while at the anode surface, I^- is converted to I_2 through the release of two electrons, such that the overall cell reaction is

$$[\text{R-2-3}] \quad 3\,I^- + I_2 \longrightarrow I_3^- + 2\,I^- .$$

Thereby one ozone molecule causes two electrons to flow in the external circuit. The electrical current is thus directly related to the uptake rate of ozone in the cathode chamber. The schematics of the ECC-ozonesonde is displayed in Figure 2-3. The Instrument, size about 8x8x14 cm, is enclosed in a styrofoam flight box (≈19 x 19 x 25 cm).

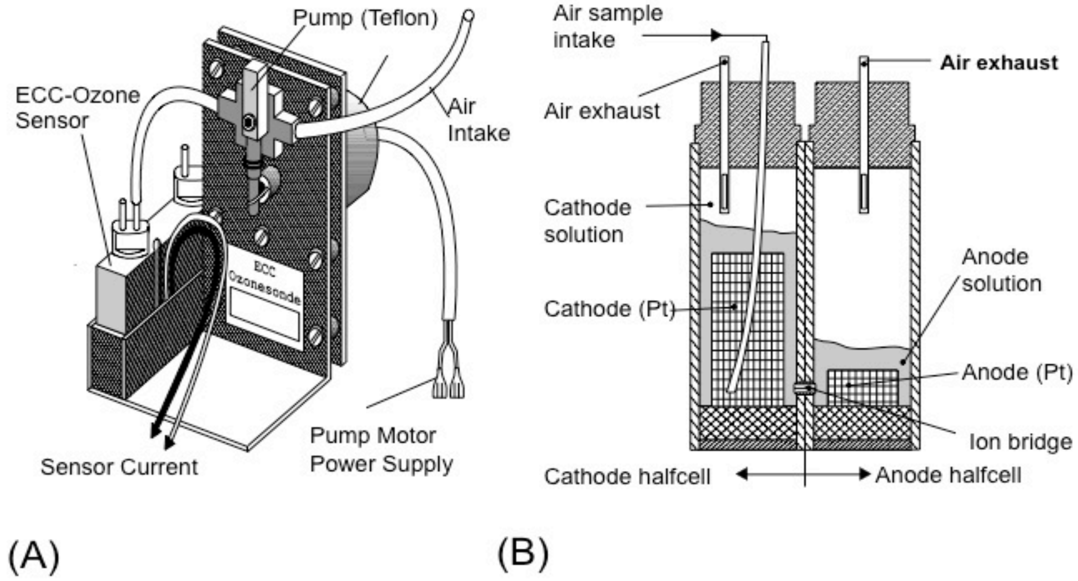

Figure 2-3: Schematics of the electrochemical concentration cell (ECC) ozonesonde (A) and sensing cell (B)

Table 2-1 lists the two different manufacturers of ECC-ozonesondes (Science Pump Corporation and Environmental Science Corporation[3]), the model production dates, and design changes [Source: *Johnson et al.*, 2002].

Table 2-1: Electrochemical concentration cell (ECC) ozonesonde models and manufacturers [Source: *Johnson et al.*, 2002]. Note: Since 2011, EN-SCI ozonesonde types are manufactured by Droplet Measurement Technologies (DMT, Boulder, USA)

Manufacturer	Model Number	Years Manufactured	Design Changes
Science Pump	1A	1968	Initial ECC ozonesonde model
Science Pump	3A	1968-1981	Rectangular pump
Science Pump	4A	1978-1995	Switch to cylindrical piston pump
Science Pump	5A	1986-1997	Start of digital data acquisition
Science Pump	6A	1995-present	
EN-SCI	1Z	1993-present	Molded plastic sensor cell

From experimental studies *Johnson et al*. [2002] found that depending on the concentrations of the cathode sensing solution, the stoichiometric ratio of the ozone to iodine conversion (R-2-1) can increase from 1 up to 1.05-1.2. Johnson showed experimentally that this increase is mostly caused by the phosphate buffer with only a minor contribution from the KI concentration. No significant influence of KBr-concentration had been observed. Table 2-2 list the three most commonly used cathode sensing solution types (SST). SST1.0 (1.0% KI & full pH-buffer) is the conventional sensing solution based on the guidelines described by *Komhyr* [1986] and is most widely used for the ozonesonde types SPC-4A, -5A, and -6A manufactured by Science Pump Corporation [1996]. SST0.5 (0.5% KI & half pH-buffer) is the sensing solution recommended by EN-SCI Corporation [1996] since 1996 as the cathode solution for their ENSCI-type of sondes. The third sensing solution SST2.0, a non-pH-buffered solution with no KBr, but

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[3] *Since beginning of 2011 Environmental Science Corporation has been taken over by Droplet Measurement Technologies (DMT, Boulder, USA)*

with 2.0% KI for the cathode cell had been introduced by *Johnson et al*, [2002] for the NOAA/ESRL ozonesonde sites which was replaced in 2007 by a 1.0% KI & 1/10th buffer solution (SST0.1).

Table 2-2: Most common sensing solution types and their chemical composition in aqueous solution for cathode cells of ECC-ozonesondes. For the anode sensing solution, usually a KI saturated cathode solution is employed

Sensing Solution Type (SST)	KI [g/L]	PH-Buffer		KBr [g/L]
		$NaH_2PO_4.H_2O$ [g/L]	$Na_2HPO_4.12H_2O$ [g/L]	
SST1.0: 1.0% KI & full buffer (a)	10	1.250	5.0	25
SST0.5: 0.5% KI & half buffer (b)	5	0.625	2.5	12.5
SST2.0: 2.0% KI & no buffer (c)	20	0	0	0
SST0.1: 1.0% KI & 1/10th buffer (d)	10	0.1250	0.5	25

(a) Komhyr [1986] , SPC-6A instruction manual [Science Pump Corporation, 1996]
(b) ENSCI-Z instruction manual [EN-SCI Corporation, 1996]
(c) Johnson et al. [2002]
(d) Johnson, private communication

2.3.2 Brewer Mast Ozonesonde (BM)

The eldest ozonesonde type still in routine operation is the Brewer-Mast sonde, which has evolved from the Oxford-Kew ozonesonde developed by Brewer and Milford in 1960. The Brewer-Mast type ozone sensor consists of a single electrochemical cell with a silver anode and platinum cathode immersed in an alkaline potassium iodide solution. A polarizing potential of 0.41 V is applied between the electrodes such that no current will flow unless free iodine is present. In operation, ozone in the sampled ambient air is forced through the sensing solution in the electrochemical cell (bubbler) to produce free iodine according redox reaction R-2-1. At the surface of the Pt-cathode, I_2 will be converted to I^- through the uptake of two electrons [R-2], while at the anode surface two electrons are released through the ionization of two silver atoms to form the insoluble silver iodide.

[R-2-4] $2\ Ag \longrightarrow 2\ Ag^+ + 2\ e$ [anode reaction]

Each ozone molecule entering the sensor causes a current of two electrons to flow through the external circuit. The original Brewer Mast ozonesonde is manufactured by Mast Keystone Corporation in Reno, Nevada, USA. A schematic diagram is shown in Figure 2-4-A. The reaction chamber (bubbler) is made of acrylic glass and contains a cylindrical platinum mesh cathode (≈6 cm^2) and a thin silver wire as anode. The bubbler is filled with 2 ml of neutrally buffered aqueous solution of potassium iodide (0.1%). The electrically driven gas sampling pump is mounted at the right side of the bubbler and forces about 220 cm^3/min of ambient air through the bubbler. The sonde is protected by a Styrofoam flight box. Elder ozone sounding stations have used mostly the BM-sonde type.

2.3.3 Japanese Ozonesonde (KC96)

The KC79/96-ozonesonde type is a modified version of the KC68-sonde type developed at the Meteorological Research Institute of the Japan Meteorological Agency (JMA) by Kobayashi and Toyama (1966). The first model KC65 was introduced to Syowa station in Antarctica in 1966, then the improved model of smaller and lighter one KC68 was introduced to Japanese remote ground observatories in 1968. Ten years later, the new model KC79 was developed by applying up-to-date electronic techniques. The latest type KC96 uses the same ozone sensor as of KC79 but applies new radiosonde unit RS2-91 and smaller styrofoam flight box.

The KC-sonde types are based on the carbon-iodine ozone sensor type (Komhyr, 1965). The ozone sensor is a single electrochemical cell containing a platinum gauze as cathode and an activated carbon anode immersed in an aqueous neutral potassium iodide solution. Phosphate buffers and potassium bromide are added to the sensing solution to keep the pH neutral, and to avoid freezing, respectively. Ozone in ambient air is bubbled through the sensing solution generating “free” iodine molecules according the redox-reaction R-2-1. At the Pt-cathode the iodine is reconverted into iodide by the uptake of two electrons, while correspondingly at the activated carbon anode under the release of two electrons following reaction takes place:

[R-2-5] $C + 2\ OH^- \longrightarrow CO + H_2O + 2e$

Accordingly, one ozone molecule produces an electrical current of two electrons in the external circuit.

A scheme of the sonde is shown in Figure 2-4-B. The gas sampling pump consists of stainless-steel piston and methacrylate resin cylinder, and the electrochemical cell are made of methacrylate resin. The pump flow rate is about 400 cm^3/min with the pump motor speed being held constant by a governor. The sonde is enclosed in a Styrofoam flight box. The RS2-KC96 sonde is manufactured by Meisei Electric Company, Gumma, Japan.

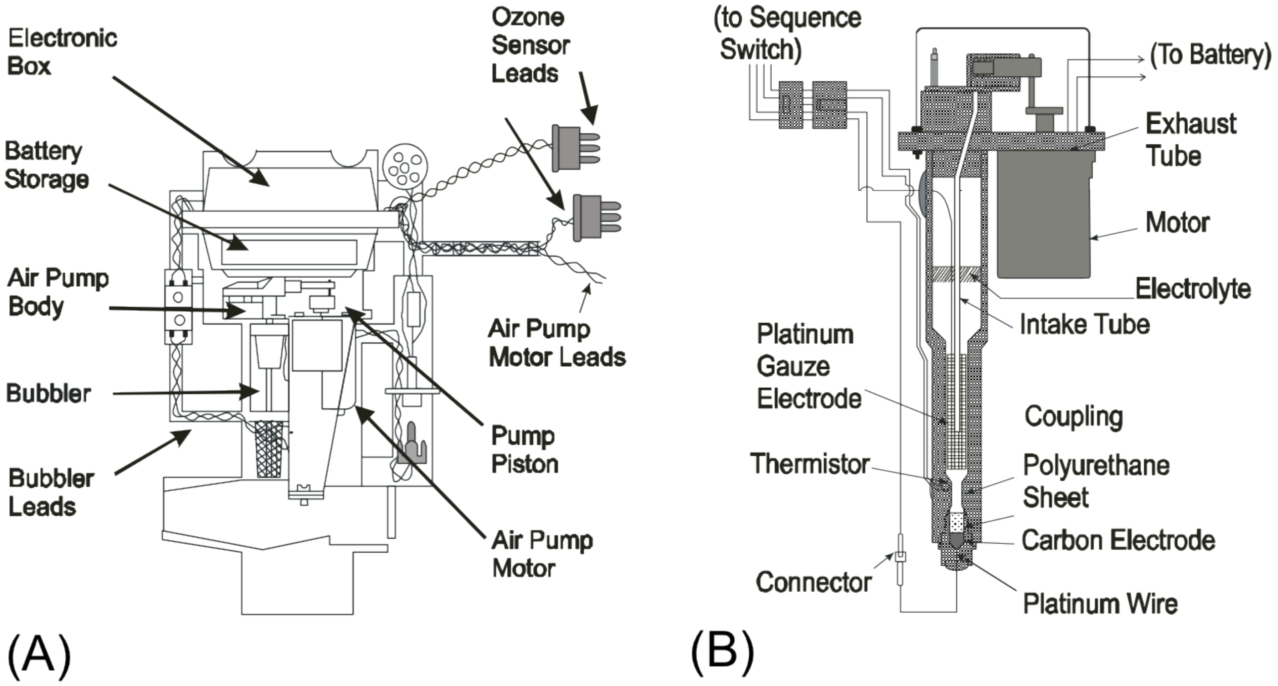

Figure 2-4: Schematics of the Brewer-Mast (BM) ozonesonde (A) and the carbon-iodine (KC96) ozonesonde (B)

3. OZONESONDE DATA QUALITY OBJECTIVES

3.1 Introduction

Electrochemical sondes were developed in the 1960's, primarily to measure ozone to study the large scale dynamics in the stratosphere. Since about 1970, after the discovery of the photochemical depletion of stratospheric ozone by chlorofluorocarbons and the photochemical increase of ozone in the troposphere, regular ozone soundings are primarily made in the GAW global network to observe long term changes of ozone. In addition, ozonesondes are an important tool for process studies or validation of satellites.

In this chapter the different aspects of data quality that can be expected from ozone soundings are presented. The objectives are twofold: (1) to guide operators and data handlers who seek objective evaluation of various techniques presently in use; (2) to explain to the larger scientific community using ozonesonde data origins of systematic variations in ozone profiles taken by different instruments and techniques. The first part deals with the major factors influencing the sonde performance and their contributions to the overall uncertainty of the measurement. The second part gives a brief review of the performance of the different sonde types in terms of precision and accuracy. The content of this chapter is for a major part based on the assessment report given by *SPARC-IOC-GAW* [1998] and updated with recent results obtained from JOSIE [*Smit et al,* 2007] and BESOS [*Deshler et al.*, 2008] intercomparison experiments.

3.2 Factors Influencing Sonde Performance

Each ozone sounding is made with a new instrument which must be characterized prior to flight. Consistency of instruments with regard to their quality and characteristics, but also standardization of operating procedures, is a pre-requisite to assure consistent sonde measurements. Several instrumental and procedural parameters (see also Eq.2-1) and their uncertainties can have a substantial influence on the quality of the ozonesonde measurements. Changes of these parameters through changes in instrument, operating procedures, or environmental conditions can have a significant impact on the long term ozone trends derived from ozonesonde measurements. From intercomparisons between different sounding stations using the same sonde type it has been shown that observed differences are, in large part, due to differences in the preparation and correction procedures applied at the different launch sites [*SPARC-IOC-GAW,* 1998, *Smit et al.*, 2007].

Although the principle of ECC sonde operation has remained the same [*Komhyr,* 1969], ECC-ozonesondes have gone through several modifications of the instrument and procedures since they were first manufactured in the early 1970's [Table 2-1, *Johnson et al.*, 2002]. These variations and their associated uncertainties can have significant effects on the sonde performance, leading to uncertainties in trend analysis [*SPARC-IOC-GAW*, 1998]. Nowadays, ECC-sondes are manufactured by either Science Pump Corporation (SPC-6A) or Environmental Science Corporation (ENSCI-Z) which was acquiredby Droplet Measurement Technologies (DMT, Boulder, USA) in 2011.

3.2.1 Instrumental Uncertainties Sonde

The partial pressure of ozone measured by the electrochemical sensor is a function of the measured sensor current (I_M), the background current (I_B), the conversion efficiency (η_C), the temperature of the gas sampling pump (T_P) and the volumetric flow rate (Φ_P):

$$[\text{E-3-1}] \quad P_{O_3} = P_{O_3}\left(\mathrm{I}_{\mathrm{M},}, \mathrm{I}_\mathrm{B}, \eta_\mathrm{C}, \Phi_\mathrm{P}, \mathrm{T}_\mathrm{P} \right)$$

The instrumental uncertainty of the electrochemical ozone sensor for the measurement of ozone is a composite of the contributions of the individual uncertainties of the different instrumental parameters listed above. Some of the contributions depend on air pressure, such that the overall uncertainty of the ozone measurement will be a function of pressure i.e. altitude.

Instrumental uncertainties are assumed to be random and following Gaussian statistics, such that applying Gaussian law of error propagation [e.g. *Bevington and Robinson,* 1992] to Eq. E-3-1 the overall relative uncertainty of P_{O3} is expressed as :

[E-3-2] $$\frac{\Delta P_{O3}}{P_{O3}} = \sqrt{\frac{(\Delta I_M)^2 + (\Delta I_B)^2}{(I_M - I_B)^2} + \left(\frac{\Delta \eta_C}{\eta_C}\right)^2 + \left(\frac{\Delta \Phi_P}{\Phi_P}\right)^2 + \left(\frac{\Delta T_P}{T_P}\right)^2}$$

From Eq.E-3-2 it is seen that the contribution of the conversion efficiency (η_C), pump flow rate (Φ_P), pump temperature (T_P) is the sum of the squares of their relative uncertainties. The contributions of the measured sensor current (I_M) and the background current (I_B) are more complicated. The square of the difference of both parameters in the denominator in equation Eq.E-3-2 indicates the sensitivity of the overall relative uncertainty of the ozone pressure to these two parameters in case that both are of the same order of magnitude.

The overall relative uncertainty of P_{O3} determined by the contributions from the individual uncertainties of the different instrumental parameters are demonstrated for an ECC type ozonesonde (Figure 3-1) for a typical mid-latitude (A) and tropical (B) vertical ozone profile. In the troposphere the overall uncertainty of P_{O3} is dominated by the contribution of the uncertainty of the background current I_B, while in the stratosphere the uncertainties of the conversion efficiency η_C and pump flowrate Φ_P are the major contributions. The different instrumental uncertainties and their influence on the overall uncertainty of P_{O3} are discussed in more detail in Sections 3.2.2 - 3.2.5.

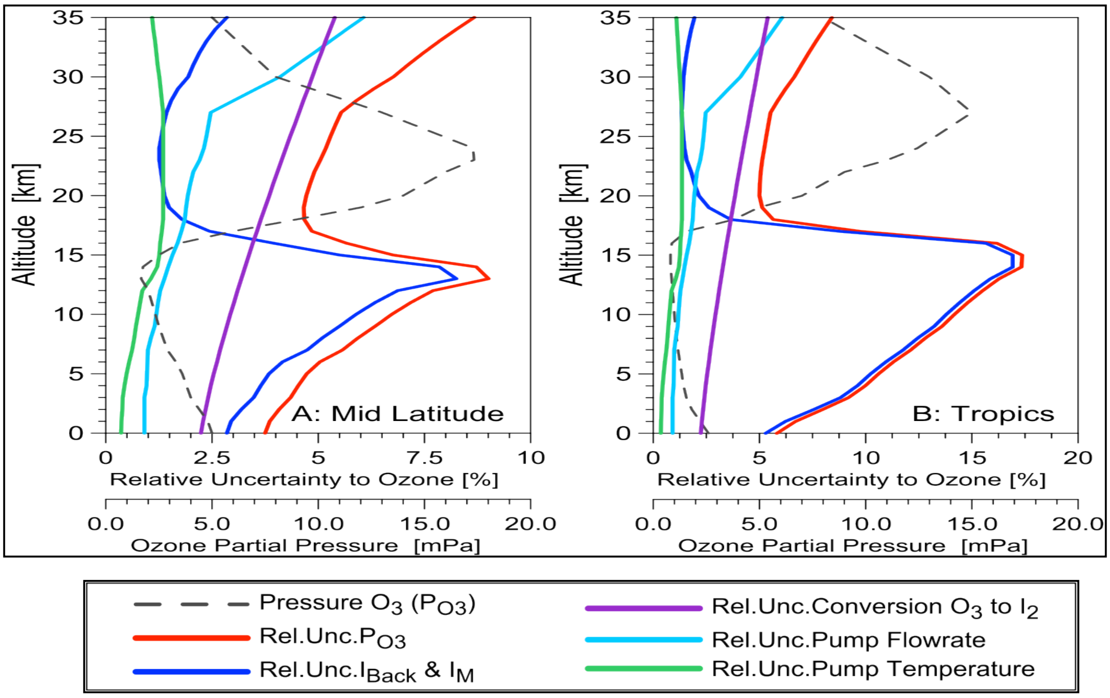

Figure 3-1: For ECC-ozonesonde type the overall relative uncertainty of P_{O3} and the contributions from the individual uncertainties of the different instrumental parameters like measured cell current (I_M=0.1-5µA, ΔI_M=±0.01µA), background current (I_B≈0.07µA, ΔI_B≈±0.04µA), conversion efficiency η_C≈1, , $\Delta\eta_C$≈±(0.05-0.07)), pump flowrate Φ_P, and pump temperature T_P as a function of altitude for a typical mid-latitude (A) and tropical (B) ozone profile. For further details see Sections 3.2.2 – 3.2.5.

3.2.2 Conversion Efficiency η_C

The conversion efficiency η_C includes both, the absorption efficiency of O_3 (α_{O3}) from the gaseous into the liquid phase of the sensing solution and the stoichiometry of the conversion of O_3 into I_2 ($S_{O3/I2}$):

[E-3-3] $\eta_C = \alpha_{O3} \bullet S_{O3/I2}$

Normally, in the pH = 7 buffered KI sensing cathode solution the stoichoimetry of the conversion reaction of ozone into iodine is 1.00 with an uncertainty of about ±0.03 [*Dietz et al.*, 1973], while the initial absorption efficiency of gaseous O_3 into the sensing solution will be 1.00 with an uncertainty of ±0.01. During normal operation both parameters are assumed to be 1.00, such that the conversion efficiency is also 1.00. However, a source of uncertainty is, that in the course of a sounding the uncertainties of the sensor cell characteristics can increase, expressed by

[E-3-4] $$\frac{\Delta \eta_{C,}}{\eta_C} = \sqrt{\left(\frac{\Delta \alpha_{O3}}{\alpha_{O3}}\right)^2 + \left(\frac{\Delta S_{O3/I2}}{S_{O3/I2}}\right)^2}$$

For example, a certain percentage of the sensing solution evaporates at a rate dependent on the temperature of the cell and the ambient pressure encountered during the sounding. Although, this evaporation will lower the amount of liquid for uptake of gaseous ozone, the absorption efficiency is not significantly affected [e.g. *Komhyr,* 1971, *Davies et al.*, 2000]. At higher altitudes this uptake is getting very efficient due to much faster mass transfer c.q. gas diffusion at lower pressures. This means that the absorption efficiency stays at 1.00, with a small uncertainty of less than 1-2 % throughout the entire profile.

Evaporation causes the concentration of the sensing solution to increase, which can enhance the sensitivity of the sensor to ozone. *Johnson et al.* [2002] showed that for ECC-sondes this increase of sensitivity is significant in presence of the „pH-buffering“ phosphate chemicals. Usually the sodium-hydrogen phosphate buffer is added to the cathode sensing KI-solution to keep the pH neutral at 7.0. However, the buffer can also be the cause for the controversy of yielding a stoichiometric factor (I2/O3) larger than unity. The reaction mechanism and stoichiometric factor (I2/O3) of the net iodometric reaction (1) has been studied by many investigators using a variety of KI-solution [e.g. *Boyd et al.,* 1970] and pH-buffers [e.g. *Dietz et al,* 1973]. It appears that depending on the concentrations of KI and the pH-buffer the stoichiometric factor can expand up to 1.25. Saltzman and Gilbert [1959] suggested that side reactions involving the phosphate buffer can lead to additional iodine and thus to an increase of the stoichiometric ratio of iodine to ozone. For BM-or KC-sondes this effect is negligible because these sondes operate at much lower concentrations of sensing solution.

However, for ECC-sondes this means that due to evaporation, the concentration of the sensing solution increases, which can enhance the sensitivity of the ECC-sensor and can increase the uncertainty of the measured ozone [*Johnson et al.* 2002, *Smit et al.,* 2007]. An increase of the stoichiometry factor $S_{O3/I2}$ during ECC ozone soundings can have significant impact on the performance of the ozonesonde by introducing uncertainties or systematic bias in the ozone measurements that can increase significantly with altitude [e.g. *Boyd et al*, 1998, *Johnson et al.*, 2002], *Smit et al.,* 2007].

Chapter 4 in the JOSIE 2000 and BESOS experiments [*Smit et al.,* 2007; *Deshler et al.*, 2008] describe significant differences in the ozone readings when ECC-sondes of the same type are operated with different cathode sensing solution strength (Table 2-2). For each ECC-manufacturer type the use of 1.0% KI and full buffer gives 5% larger ozone values compared with the use of 0.5% KI and half buffer, and as much as 10% larger values compared with 2.0% KI and no buffer [Smit et al., 2007]. JOSIE demonstrated that the performance characteristics of the two ECC-sonde types can be significantly different, even when operated under the same conditions. Particularly above 20 km the ENSCI-Z sonde tends to “measure” 5-10 % more ozone than the

SPC-6A sonde. Below 20 km the differences are 5 % or less, but appear to show some differences with year of manufacture.

In the uncertainty analysis shown in Figure 3-1 the uncertainty of the conversion efficiency is estimated according Eq. 3-5: The uncertainties at the surface ($\Delta\ \alpha_{O3} \approx \pm 0.01$ and $\Delta\ S_{O3/I2} \approx \pm 0.02$) increase linearly with altitude to $\Delta\ S_{O3/I2} \approx \pm 0.05$ at Z=35 km.

Another potential source of uncertainty is the influence of local air pollution which can have detrimental effect on the conversion efficiency, i.e. sensor performance. Ozone measurements by a KI-method, like the electrochemical ozone sensor, is sensitive to interferences by oxidizing or reducing agents [*Schenkel et al.*, 1982]. However, several laboratory experiments show that normally for moderately polluted air, sulphur dioxide (SO_2) is the only trace gas which can give significant negative interferences in the measurements of ozone. As a reducing agent, SO_2 converts the produced iodide from the ozone/iodine-reaction back to iodine. A memory effect can occur if an excess of SO_2 is accumulated (as bi-sulphite and sulphite ions) in the sensing solution of the sensor which could affect not only measurements in the polluted boundary layer itself but also several km above [*Schenkel et al*. 1982] and can deteriorate significantly the lower part of the measured vertical ozone profile [*De Muer and De Backer*, 1993].

3.2.3 Cell Current I_M and Background Current I_B

The uncertainty of the measured sensor current (I_M) is mainly determined by the accuracy of the current measurement by the electronics (current (I) to voltage (V) converter) of the sonde data interface board such that for currents above 1 μA the uncertainty of I_M is about ±1 percent of the measured value, while for currents below 1 μA the uncertainty will be about ±0.01 μA.

Prior to balloon launch the background current of each ozonesonde is individually determined. Excepted are the Brewer-Mast sondes where prior to flight the sonde readings are electronically compensated for the background current. Background signals determined at the surface are typical in the range of 0.1-0.5 mPa ozone equivalent. Ozone soundings are thus sensitive to errors in the background signal correction in regions where the ozone concentration is low, i.e. upper troposphere. Such errors have the potential to become large in case that the background signal is similar in magnitude to the ozone signal. This is particularly important in the tropics, but also in the polar regions in case of strong polar stratospheric ozone depletion [*Voemel and Diaz*, 2010].

To demonstrate the impact of background current on tropospheric ozone measurements Figure 3-2 shows the influence i.e. fraction of the background current to the measured ozone current as a function of altitude for ozone profiles that are typically encountered at mid latitudes (left diagram) and in the tropics (right diagram), respectively.

Figure 3.2 indicates that the contribution of the background current, at typical values of 0.05-0.1 μA to the measured current with typical values of 0.2-1 μA (=0.7-4 mPa ozone) in the troposphere, is large enough to have a significant influence on the accuracy of the ozone measurements, especially in the middle and upper troposphere. In particular, tropical ozone profiles with extremely low ozone values in the middle and upper troposphere [e.g. *Kley et al.,* 1996] are strongly influenced by the magnitude of the background current and its accuracy [*Smit et al.,* 1994, *Reid et al.,* 1996].

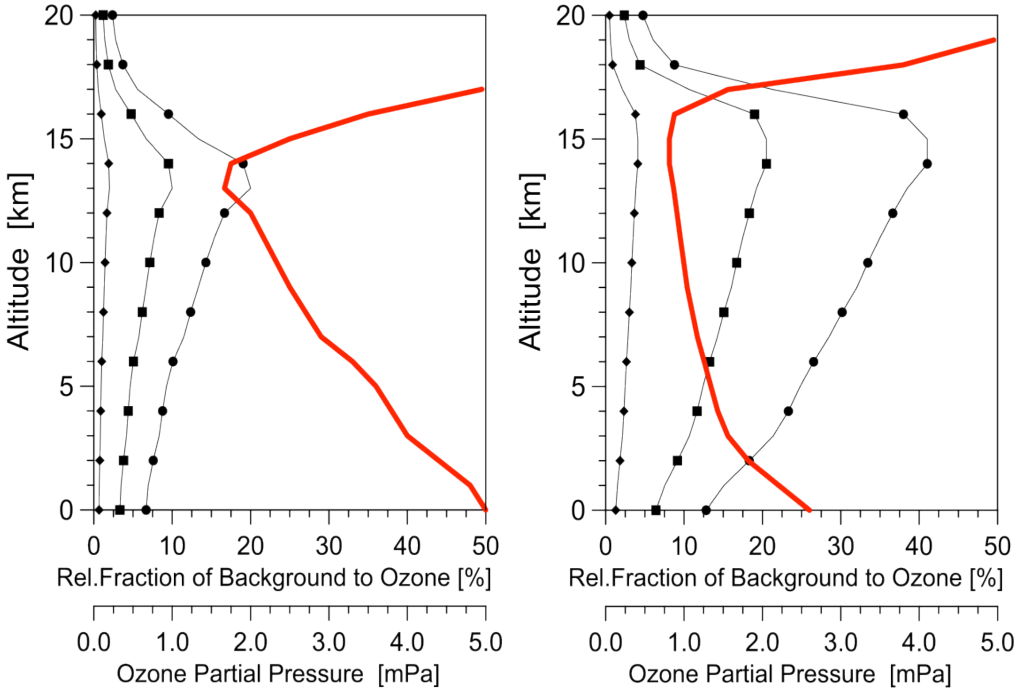

Figure 3-2: Contribution of the background current of the ECC-ozone sensor as a relative fraction of the vertical profile of ozone (solid red line im mPa) for background values of 0.01 µA (◆), 0.05 µA (■) and 0.1 µA (●) at mid-latitudes (A) and in the tropics (B)

In the conventional method of background correction for ECC-sondes it is assumed that the background current is pressure dependent, c.q. proportional to the oxygen partial pressure, such that this offset declines proportionally with decreasing pressure P implying to be small in the upper troposphere and getting minimal in the stratosphere:

[E-3-5] $$I_B = I_{B0} \times \frac{P}{P_0}$$

where I_{B0} is the background current measured during pre-flight preparations at surface pressure P_0.

Laboratory studies with ECC-sondes [*Thornton and Niazy*, 1982, 1983; *Smit et al.*, 1994] did not confirm any oxygen dependence on the background current and suggested to apply a constant background current correction throughout the entire ozone profile.

Nowadays background currents are typically varying between 0.03-0.11 µA (Table 3-1) such that in order to estimate its impact on the uncertainty on P_{O3}, as displayed in Figure 3-1, an average value of 0.07µA with an uncertainty of ±0.04 µA for I_B has been assumed. From Figure 3-1 it is obvious that the uncertainty in the background current is dominating the uncertainty of the ozone measurement in the troposphere, particularly in the Tropics. The uncertainty of the background current is for a large part due to the poor understanding of its origin, preventing a physico-chemical description and how to correct for.

Results from JOSIE 1998 [*Smit and Straeter,* 1994] indicated that the background signal is correlated with past exposure to ozone. As a consequence, it was recommended to measure the background current before and after exposure of ozone in the pre-flight preparation procedures, which was shown during JOSIE (Table 3-1; *Smit et al.,* 2007). Although the background currents of the SPC-6A and ENSCI-Z sondes are of the same magnitude, they both are significantly larger after exposure to ozone. This enhancement effect of the background current, from values 0-0.05

µA before ozone exposure to 0.05-0.11 µA after exposure to ozone, is poorly understood [*SPARC-OTA-GAW,* 1998].

The background current is not a time invariant ECC-property but at a defined time it is the result of a minor but still slowly decaying contribution to the measured cell current (See Figure 3.3). Based on laboratory experiments *Voemel and Diaz* [2010] suggested that this is most likely due to the fact that the ECC-chemistry has a fast but also an additional minor and slow reaction pathway (reaction time constant typically 20-30 min) causing a memory effect due to slow side reactions in the oxidation of iodide by ozone in the cathode sensing solution. In equilibrium this leads to an overall stoichiometry factor, $S_{O3/I2}$, larger than 1.0. The magnitude of this excess stoichiometry effect is strongly related to the strength of the phosphate buffer concentration in the cathode sensing solution (See Section 3.2.2). Voemel and Diaz [2010] suggested therefore that instead of a measured background current it would be better to use appropiate solution dependent conversion efficiency and background current values in the basic ECC-formula (Eq E-2-1). In order to follow this new approach of post flight processing more research is needed.

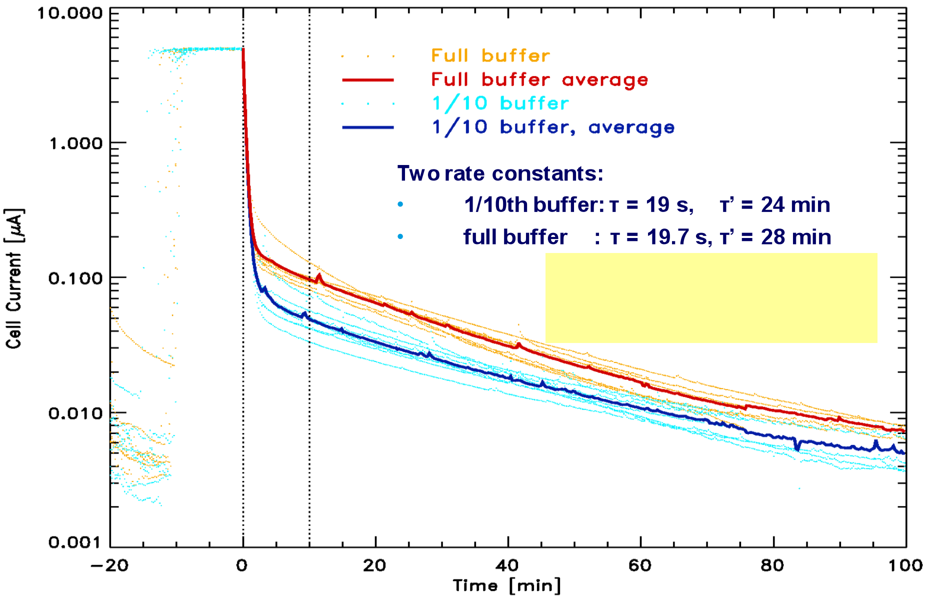

Figure 3-3: ECC-ozone sensor current with purified air as function of before, during and after the ECC-sensor has been exposed to about 170 ppbv ozone (~5µA cell current) for about 10 minutes. ECC-sensor were charged with either 1%KI, full buffer (SST1.0) or 1%KI, 0.1(1/10) buffer. Source: *Voemel and Diaz* [2010]

For an improved ECC data processing the contributions of the slow (20-30 min) as well as the fast (20-30 s) responses to the overall measured ECC ozone signal need to be considered simultaneously through the use of an appropriate response (memory) function. Such a possible method may be the deconvolution of the measured ozone profile after determining the overall frequency response of the combined sensor and air sampling system [*De Muer and Malcorps*, 1984]. However, more research on this topic is needed to overcome the problem of the ECC-sensor response with the fast and slow signal component.

It is obvious, because the timed background measurement is directly correlated to the ozone exposure of the ECC-sensor, the concept of a constant timed background I_B should be treated with caution. Although, there is no scientific justification to record the background current after 10 minutes exposure with ozone free air, it is still part of the SOP's to record the background currents before and after exposure with ozone during the pre-flight preparation of the sonde and just prior to launch (I_{B0},I_{B1} and I_{B2} respectively). At the present, as kind of interim solution, the ASOPOS-panel recommends to use a constant, pressure independent I_{B2} to use in basic equation Eq. E-2-1 to determine the ozone partial pressure throughout the entire vertical profile.

Table 3-1: Survey of average background current (±1σ) before and after exposure of ozone obtained during pre-flight preparations of ECC-sondes "flown" during JOSIE 1996, 1998 and 2000 [Smit et al., 2007]. The background currents were recorded before and after pumping for 10 minutes air with ozone (150-200 ppbv) through the sensor whereby each time before the background current was measured the sensor was flushed for ten minutes with ozone free air

ECC-Sonde Type		ENSCI-Z		SPC-6A	
JOSIE	Sensing Solution Type	Background Current Before O_3-Exposure [μA]	Background Current After O_3-Exposure [μA]	Background Current Before O_3-Exposure [μA]	Background Current After O_3-Exposure [μA]
1996	SST1.0	0.05±0.01	0.07±0.02	0.02±0.01	0.07±0.01
1998	SST1.0	0.05±0.02	0.11±0.03	0.03±0.02	0.11±0.01
2000	SST1.0	0.02±0.03	0.06±0.05	0.02±0.01	0.05±0.02
2000	SST0.5	0.02±0.02	0.05±0.02	0.00±0.01	0.03±0.02
2000	SST2.0	0.02±0.02	0.06±0.03	0.02±0.01	0.05±0.03
Background current [μA]		0.02-0.05	0.05-0.11	0.00-0.03	0.03-0.11
Background contribution to ozone partial pressure [mPa]		0.07-0.17 mPa	0.2-0.4 mPa	0-0.1 mPa	0.1-0.4 mPa
Background contribution to surface ozone at mid latitude		2-5 %	2-10 %	0-3 %	3-10 %

3.2.4 Pump Flow Efficiency

The volumetric flow of the gas sampling pump of each sonde is individually measured at the ground before flight. The pump flow rate of the sonde is usually measured with a bubble flow meter at the gas outlet of the sensing cell. Before the sampling air is forced through the sensing solution and entering the bubble flow meter it is usually "non-saturated": (RH<100%) or even generally "dry" (RH=0%). Evaporation of water in the sensing solution or in the bubble flow meter increases the actual flow rate of the air forced through the pump. Therefore, the measured flow rate have to be corrected for this "moistening effect" to yield the actual pump flow rate according to the following formulas:

[E-3-6] $$\Phi_{Pump,Actual} = \Phi_{Meas} \bullet \left[\frac{\left(P_{Lab} - \Delta P_{H_2O}\right)}{P_{Lab}}\right]$$

[E-3-7] $$\Delta P_{H_2O}\left(T_{Lab}\right) = \left[1 - \frac{RH_{Air}}{100}\right] \bullet P_{H_2O,Sat}\left(T_{Lab}\right)$$

[E-3-8] $$\Phi_{Pump,Actual} = \Phi_{Meas} \bullet \left[1 - \left[1 - \frac{RH_{Air}}{100}\right] \bullet \frac{P_{H_2O,Sat}\left(T_{Lab}\right)}{P_{Lab}}\right]$$

Whereby:

Φ_{Meas} = Pump flow rate measured with bubble flow meter [ml/min].
$\Phi_{Pump, Actual}$ = Actual pump flow rate after correction for "moistening effect" [ml/min].
P_{Lab} = Air pressure laboratory [hPa]
T_{Lab} = Air temperature laboratory [K]
$\Delta P_{H2O}(T_{Lab})$ = Water vapour partial pressure [hPa], contribution due to evaporation in the sampling air at T_{Lab}.

RH_{Air} = Relative Humidity of the sampled air at the intake of the pump [%]
$P_{H2O,Sat}(T_{Lab})$ = Saturated water vapor pressure at T_{Lab} [K] or t_{Lab} [^oC]. There are several empirical formulas, such as by Magnus-Teten [*Murray*, 1967]:

[E-3-9] $$Log_{10}\left(P_{H2O,Sat}\right)=\frac{\left(7.5\bullet t_{Lab}\right)}{\left(t_{Lab}+237.3\right)}+0.7858$$ (See also Table 3-2)

Note: t_{Lab} is laboratory air temperature in degrees Celsius [^oC] !

Table 3-2: Water vapour saturation pressure over liquid water determined after empirical formula by Magnus-Teten [*Murray,* 1967]

Temperature [^oC]	$P_{Sat,H2O}$ [hPa] After Magnus-Teten [*Murray, 1*967]
0	6,1
5	8,7
10	12,3
15	17,1
20	23,4
25	31,7
30	42,4
35	56,2
40	73,7
45	95,8
50	123,3

After correction of the pump flowrate for the "moistening effect the uncertainty $\Delta\Phi_P$ of the volumetric pump flow rate at the ground is determined primarily by the accuracy (±2 ml/min) of the soap film displacement measuring technique itself. This means that for a volumetric flow rate of about 200-230 ml/min the relative contribution of the uncertainty of the flow rate determination will be below ±1 %.

At ambient air pressures below 100 hPa the efficiency of the gas sampling pump degrades due to pump leakage, dead volume in the piston of the pump, and the back pressure exerted on the pump by the cell solution [*Komhyr*, 1967, *Steinbrecht et al.*, 1998]. This decrease in pump efficiency at reduced pressures is corrected for by applying a pump correction factor C_{PF}, which is as function of ambient pressure specific for each sonde type:

[E-3-10] $$\Phi_P=\frac{\Phi_{P,\,Ground}}{C_{PF}}$$

Typical correction factors C_{PF} as a function of ambient pressure for each ozonesonde type are listed in Table 3-3.

The relative uncertainty of the effective volumetric pump flow rate Φ_P, which is determined by the contributions from the uncertainty of the determination of the flow rate $\Phi_{P,Ground}$ at the ground check and the uncertainty of the pump flowrate correction factor C_{PF} at lower air pressures, can be expressed by applying equation E-3-10 as:

[E-3-11] $$\frac{\Delta \Phi_{\mathrm{P}}}{\Phi_{\mathrm{P}}} = \sqrt{\left(\frac{\Delta \Phi_{\mathrm{P,\,Ground}}}{\Phi_{\mathrm{P,\,Ground}}}\right)^2 + \left(\frac{\Delta C_{\mathrm{PF}}}{C_{\mathrm{PF}}}\right)^2}$$

The uncertainty ΔC_{PF} of the pump efficiency correction factor for ECC-sondes is assumed to be about half of the differences between the lower and upper limit of the pump efficiencies as determined by *Komhyr* [1986, 1995] and *Johnson et al.* [2002] listed in Table 3-3.

The correction tables are based on empirical averages obtained from pump flow efficiency measurements made at different air pressures in the laboratory [*SPARC-IOC-GAW,* 1998]. The uncertainty of the correction factors presented increases substantially at pressures below about 20 hPa which can contribute significantly to the overall uncertainty of the sonde performance above 25-30 km altitude. The uncertainty of the pumpflow efficiency is one of the most prominent contributions to the overall uncertainty of the sonde measurements above 25 km altitude.

Table 3-3: Pump flow correction factors (C_{PF}) as a function of air pressure for (i) ECC-ozonesondes reported by *Komhyr,* 1986, *Komhyr et al.,* 1995, and *Johnson et al*, 2002; (ii) Brewer Mast ozonesonde reported by *Steinbrecht et al.*, 1998; (iii) Carbon iodine (KC96) ozonesonde [*Kobayashi and Toyama,* 1966]

Pressure [hPa]	ECC *Komhyr,* 1986	ECC *Komhyr et al.,*1995	ECC *Johnson et al.,*2002	BM *Steinbrecht et al.,*1998	KC96 *Kobayashi et al.,*1966
1000	1	1	1	1	1
100	1,007 ± 0.005	1,007 ± 0.005	1,035 ± 0.011	1,027 ± 0.004	1.02
50	1,018 ± 0.006	1,018 ± 0.005	1,052 ± 0.012	1,075 ± 0.006	1.04
30	1,022 ± 0.008	1,029 ± 0.008	1,072 ± 0.015	1,108 ± 0.007	1.07
20	1,032 ± 0.009	1,041 ± 0.012	1,088 ± 0.018	1,150 ± 0.011	1.11
10	1,055 ± 0.010	1,066 ± 0.023	1,145 ± 0.020	1,280 ± 0.020	1.25
7	1,070 ± 0.012	1,087 ± 0.024	1,200 ± 0.025	1,5 ± 0.1	1.40
5	1,092 ± 0.014	1,124 ± 0.024	1,260 ± 0.030	1,8 ± 0.2	1.66

3.2.5 Temperature of Gas Sampling Pump

To correct for changes of the air mass flow rate through the sensor due to temperature changes the actual pump temperature is measured in-flight either inside the pump or in the instrument enclosure (Styrofoam box). Over the course of a sounding the pump temperature can decline typically by 10-25°C. However, in most of the earlier sounding systems used before the 1990's it was not possible to measure the actual pump temperature due to the limited number of signals the analog operating radiosondes were capable of transmitting . Therefore, it was common practice that either a constant pump temperature or an empirical table of the pump temperature as a function of ambient air pressure was applied. This can introduce uncertainties of 1-7% in the ozone computations, particularly for the highest altitudes [*SPARC-OTA-GAW*, 1998].

Although, in modern soundings the temperature itself can be measured with an accuracy better than 1-2 K, the location of the pump temperature sensor can be still an additional source of uncertainty. From a series of field ECC-soundings *O'Connor et al.,* (1998) showed that temperatures measured inside or outside the pump can differ significantly, from values of ≈1K near the surface and increasing up to values of ≈5-10K at lower pressures. A common procedure for measuring the pump temperature was to tape a thermistor to the outside of the Teflon block of the pump near to and at the same height as the tube outlet from the block (going to the cathode cell) - henceforth known as the 'external pump temperature'. Nowadays, both ECC-sonde manufacturers provide their sondes with a hole drilled into the Teflon block. This allows the thermistor to be positioned close to the piston and to measure the 'internal pump temperature'.

For ECC sonde types the effect on calculated ozone of measuring temperature inside or outside the pump is illustrated in Figure 3-4 showing the typical evolution of the internal and external pump temperatures as a function of pressure [*Smit et al.,* 2007]. Due to frictional heating of the moving piston of the pump the internal pump temperatures are higher than the external pump temperature. At lower pressures the differences are larger through declining convective heat exchange between the pump surface and the air inside the Styrofoam box., Using the internal pump temperature instead of the external pump temperature can lead to 0-3% larger ozone readings depending on pressure, i.e. altitude (Figure 3-4) [*Smit et al.*, 2007]. However, it is to be noted that the different placement of the temperature sensor does not affect in any way the current measured. Here the uncertainty ΔT_P of the pump temperature is estimated be about half of the differences between the internal and external temperature as a function of altitude.

From Figure 3-1 it is obvious that in case of modern soundings the contribution of the uncertainty of the pump temperature is of minor importance to the overall uncertainty for P_{O3}, primarily due to consistent placement of the pump temperature sensor within the Teflon block by the ECC manufacturers.. Sources of significant uncertainties remain if not well defined temperatures (e.g. box or sensing solution) are used as pump temperature in Eq.2-1 to derive ozone.

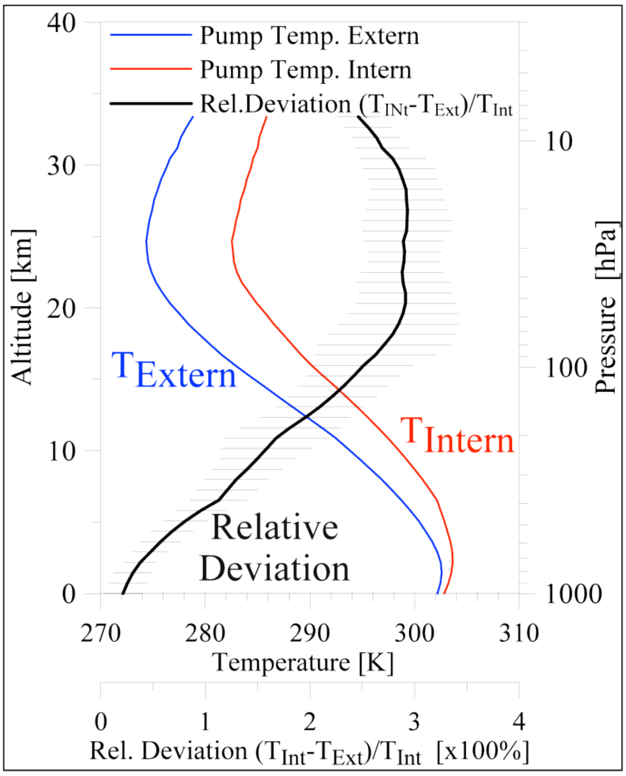

Figure 3-4: Internal and external pump temperature and their relative differences as a function of altitude (i.e. pressure) obtained from combined internal and external temperature measurements over an ensemble of 8 ECC-sondes (3 ENSCI-Z and 5 SPC-6A) tested during JOSIE 2000 [*Smit et al.,* 2007]

3.2.6 Sensor Response Time

The in-flight response time(4) to a step change is approximately 20-30 s for the ECC-and BM-sonde, and 40-50 s for KC96 sonde [*Smit and Kley,* 1998]. At a typical ascent velocity of 5m/s this translates into an altitude resolution of about 100 m for ECC and BM and 200 m for KC96 and a slight displacement of the profile in the vertical relative to the actual profile. The usual practice is to make no correction for the lag in response. Further, it is to be noted that the ECC sonde signal consists of an second minor component with a much slower response time of 20-30 min (Figure 3.3) [e.g. *Voemel and Diaz*, 2010]. This second component is strongly related to the concentration

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[4] *The response time τ_{Res} on a downward step is defined as the time required for the signal S(t) to decay by a factor 1/e of its initial value S(0) , whereby S(t) = S(0) * Exp[-t/τ_{Res}]*

of the phosphate buffer in the cathode sensing solution and can have a significant effect on the ECC-sonde data (See Section 3.2.2 and 3.2.3)

3.2.7 Total Ozone Normalization

As a mean for evaluating the quality of a sonde measured ozone profile, the integrated column amount is compared with an independently determined ozone column amount [*SPARC-OTA-GAW*, 1998]. Usually this is expressed in the so called total ozone normalization factor (N_T), i.e. ratio of an independent nearby total ozone column measurement by e.g. a Dobson or Brewer spectrophotometer (Ω_C) and total ozone column derived from ozonesonde profile (Ω_T):

[E-3-12] $$N_T = \frac{\Omega_C}{\Omega_T}$$

The total ozone column from sonde (Ω_T) consist of the integrated column of ozonesonde profile (Ω_S) plus an estimated residual ozone column (Ω_R) above the burst altitude (Z_B):

[E-3-13] $$\Omega_T = \Omega_S + \Omega_R$$

The integrated column of sonde profile is:

[E-3-14] $$\Omega_S = \int_{Surface}^{Burstlevel} n_{O3}(z) \cdot dz = \sum_{z_i = Surface}^{z_i = Burstlevel} n_{O3}(z_i) \cdot \Delta z_i$$

whereby $n_{O3}(z)$, cq. $n_{O3}(z_i)$ are either ozone concentration from sonde at altitude z or z_i, respectively.

The estimated residual ozone column above burst level until top of atmosphere (TOA) is:

[E-3-15] $$\Omega_R = \int_{Burstlevel}^{TOA} n_{O3}(z) \cdot dz = \sum_{z_i = Burstlevel}^{z_i = TOA} n_{O3}(z_i) \cdot \Delta z_i$$

Ozone column abundances are usually expressed in Dobson units, whereby 1 DU= 2.69×10^{16} molecules ozone per cm^2 at STP (Standard Temperature (=273.15 K) and Pressure (=1013.25 hPa) conditions.

Several procedures have been developed to calculate the residual ozone column (Ω_R) above burst altitude. The eldest standard procedure for calculating the residual ozone column (Ω_R) is to assume a residual column with constant mixing ratio (CMR) equal to the measured value at the top of the sonde profile. Although still in common use, satellite observations have shown that the ozone mixing ratio declines above about 35 km [*SPARC-OTA-GAW*, 1998]. Uncertainties in the sonde readings of pressure and ozone at the burst altitude, and also the assumption of constant mixing ratio, can introduce significant uncertainties in the estimation of the residual ozone column [e.g. *Jeannet et al.*, 2007]. This can be improved by an alternative method in which a climatology of residual ozone column data obtained from satellite observations is used [*McPeters et al.,* 1997, 2007]. However, the influence of uncertainties in pressure readings at the bursting point remains.

The CMR method tends to overestimate the residual ozone column (Ω_R) and depending on the burst altitude of the sonde this will consequently yield into a normalization factor value that is about 2-4 percent too low [*McPeters et al.,* 1997]. For well-calibrated UV spectrometers the standard uncertainty of direct sun total ozone measurements is better than ±3% [*Basher,* 1982] until 1990s, while nowadays uncertainties better than ±2% can be yielded [*SPARC-IOC-GAW*, 1998].

Optionally ozonesonde profiles are normalized, whereby the ozonesonde profile is linearly scaled by the total ozone normalization factor (N_T). The use of the normalization to adjust the profile is controversial due to the fact that the electrochemical ozonesonde is in principle an absolute measuring device. The linear scaling of an ozone profile should only be done after making all known altitude dependent corrections to the profile. Normalization of the profile may provide stability to the ozone time series in the altitude region between 20 and 30 km containing the major fraction of the total ozone amount [*Fioletov et al.*, 2006]. However, it also produces some risks that regions with smaller ozone amounts (the troposphere and above 30 km) will be adversely affected if altitude dependent corrections are not adequately known [*SPARC-IOC-GAW,* 1998].

Even if the total ozone normalization factor is not used to correct the sonde profile it still provides a good screening test for unreliable soundings using the criterion that the normalization factor may not deviate more than about ±(0.1-0.2) from one [*Tiao et al.,* 1986]. However, a normalization factor of one is not a guarantee that the profile is correct. In routine operation the normalization factors for ECC-sondes are in the range of 0.9-1.1 while BM-and KC-sondes show normalization factors of 0.8-1.2 [See Figure 3-4].

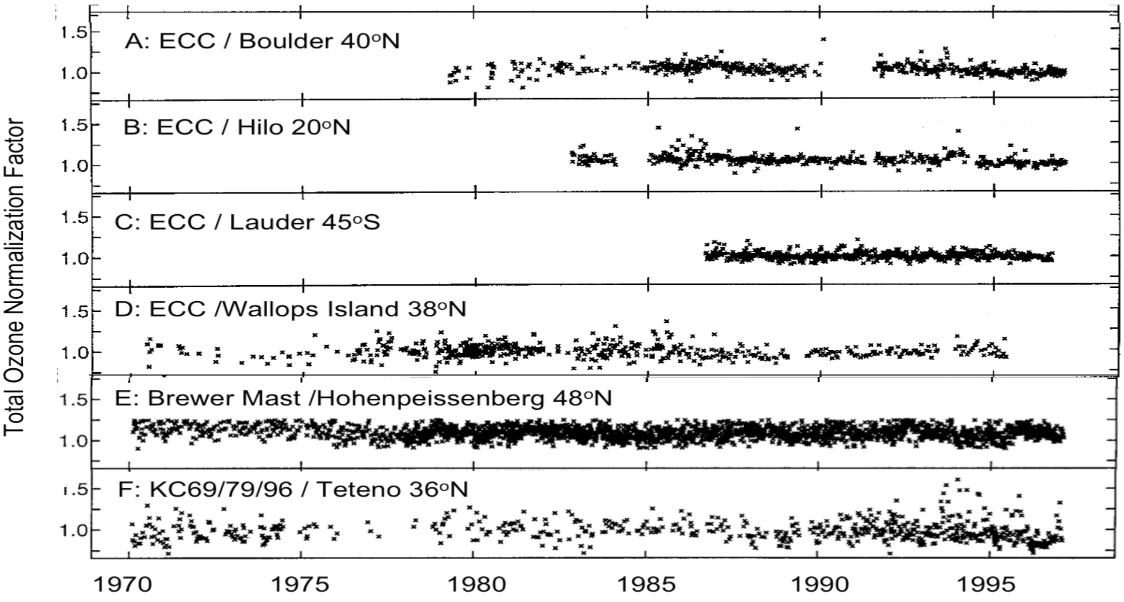

Figure 3-5: Examples of long term variations of total ozone normalization factors for different ozonesonde types: ECC (A, B, C, D), Brewer Mast (E) and KC-68/79/96 (F). Source: *SPARC-IOC-GAW Assessment of Trends in the Vertical Distribution of Ozone* [1998]

3.3 Performance of the Sondes

To assess the performance of the sondes and to quantify any systematic differences among the various sonde types, several intercomparisons have been carried out since 1970 [e.g. *SPARC-IOC-GAW*, 1998]. The earlier intercomparisons [*Attmanspacher and Dütsch*, 1970, 1981; *Kerr et al.,* 1994], included only ozonesondes, without comparisons to a reference profile measured by a separate technique. Other intercomparisons [e.g. *Hilsenrath et al.*, 1986; *Aimedieu et al.,* 1987; *McDermid et al.*, 1990; *Komhyr et al.*, 1995; *Beekmann et al.*, 1994, 1995] used a reference profile measured by other techniques. Results of these intercomparisons yield better estimates of absolute errors for the sonde measurement as a function of altitude.

To quantify the precision and accuracy of the three different types of ozonesondes since 1970 several comparison studies of sondes with other ozone profiling techniques have been made. Most intercomparison studies, particularly before 1990, focussed exclusively on sonde performance in the stratosphere. However, due to the much lower concentrations of ozone in the troposphere compared to the stratosphere the performance of the sondes and their typical instrumental and operational factors determining precision and accuracy are rather different in the two regions of the atmosphere. Since the 1990's investigations have been completed to address the performance of ozonesondes in the troposphere [*Beekmann et al.,* 1994, 1995; *Reid et al.,* 1996; *Ancellet and Beekmann*, 1997; *Tarasick et al*., 2002; *Johnson et al.,* 2002].

These short term intercomparisons are more or less "snap shots" and may not necessarily reflect the performance of ozonesondes under operational field conditions. Long-term comparison studies of ozonesonde data with other simultaneously operating ozone monitoring devices like lidar or microwave are more suitable to assess the data quality of the ozonesonde measurements in regular operation. In addition, intercomparisons like the series of JOSIE experiments [*Smit et al*., 2007] conducted in a controlled environmental chamber capable of simulating real sounding conditions, where an UV-photometer serves as reference, address specific questions. In conjunction with field intercomparisons like BESOS [*Deshler et al*., 2008] they permit the investigation and characterization of ozonesonde performance more systematically. The recent JOSIE and BESOS experiments and the ASOPOS initiative will improve the homogeneity and quality of ozone sounding data and ensure more confidence in the observed trends.

An comprehensive review of the performance of ozonesondes in terms of precision and accuracy is given in *SPARC-IOC-GAW Assessment of Trends in the Vertical Distribution of Ozone* [1998]. The assessment also showed inconsistencies in trends derived from data gathered from different sounding stations. Table 3-3 show a summary of the precision and accuracy of the different types of ozonesondes over 5 km altitude bins from the surface up to 35 km. The presented data are a synthesis obtained from *SPARC-IOC-GAW* [1998], JOSIE [*Smit et al.,* 2007] and BESOS [*Deshler et al.,* 2008] and will be discussed in the next Sections in more detail. Precision here is confined to reproducibility or repeatability and can be characterized in terms of the standard deviation of the sonde measurements when exposed to the same ozone input. Precision is related to random errors of the sonde. This in contrast to bias, which is the difference of the sonde from an ozone reference instrument and is associated with systematic errors of the sonde. Accuracy is here defined as the sum of bias and precision. The precision and accuracy here listed obtained from experimental intercomparison fits within the theoretical estimate of the overall relative uncertainty of an ozonesonde described in Section 3-2.

3.3.1 Stratospheric Performance

In general all intercomparison studies, short-term as well as long- term studies, have indicated that in the lower to middle stratosphere between the tropopause and ~ 28 km the three different sonde types show consistent results provided the individual measured sonde profiles have been normalized to ground-based total ozone column measurements at the launch site. This can be understood knowing that the normalization is mainly weighted to the ozone in the lower stratosphere which contains most of the column ozone. In this altitude range the precision of the various sonde types is within ±3 %, while any systematic biases compared to other ozone sensing techniques are smaller than ±5 %.

For altitudes above 28 km the results are not so conclusive and the responses of the sondes are different and cannot be generally characterized. The Brewer-Mast sonde used by the established (long-term record) stations (e.g. Hohenpeissenberg) show systematic underestimation of ozone which increases with altitude (-15 % at 30 km). For the ECC-sondes, there is some evidence suggesting that measurements agree with each other and to reference techniques to within ±5 %. The Japanese KC79/96 tends to overestimate ozone above 30 km. The data quality of sondes above 28 km is strongly influenced by the decreased efficiency of the air sampling pump at lower pressures, and possible increased sensitivity of the sonde to ozone due to an increase of the stoichiometry of the reaction of O_3 with KI in presence of the buffer. However, most of the intercomparison studies show that the performance of the ECC sondes between 28 and 35 km is still rather good and tends even to overestimate the ozone compared to lidar measurements. For ECC-sondes there is some experimental evidence suggesting that due to evaporation, the concentration of the sensing solution increases which can enhance the sensitivity to ozone (see Section 3.2.3) , thus compensating for reduced pump efficiency [*Johnson et al*., 2002, *Smit et al.,* 2007]. However, in general the sonde data above about 28 km are less reliable and should be used with caution, particularly for the non-ECC-sonde types.

3.3.2 Tropospheric Performance

Laboratory and field experiments have attempted to assess the reliability of the ozonesonde instrument [*Powell and Simmons*, 1969; *Reid et al.,* 1996; *Tarasick et al.,* 2002; *Smit et al.*, 2007; *Thompson et al.,* 2007c, *Voemel and Diaz*, 2010], and ozonesonde field intercomparison campaigns have been conducted [*Attmannspacher and Dütsch,* 1970, 1981; *Hilsenrath et al.,* 1986; *Beekman et al*., 1994; *Kerr et al.*, 1994; *Margitan et al.,* 1995; *Deshler et al.*, 2008; *Stübi et al.,* 2008]. In general these indicate that in the absence of significant concentrations of interfering gases, ECC ozonesondes have a precision of 3-5% and an absolute accuracy of about 10% in the troposphere, since differences in sonde manufacture and preparation introduce tropospheric biases of ~±5%.

However, because ozone concentrations in the troposphere are lower than in the stratosphere, the impact of instrumental errors and variability is larger. As a result, the historical WOUDC record shows larger uncertainties at the surface and near the tropopause [Liu et al., 2008], as do field experiments [*Kerr et al,* 1994; *Deshler et al.,* 2008; *Stübi et al.,* 2008]. Interference from other gases can be a problem in polluted areas: SO_2 has an inverse effect on the cell chemistry, cancelling ozone mole for mole, while NO_2 has a much smaller, positive effect [*Schenkel and Broder,* 1982; *Tarasick et al.,* 2000]. Although in the past Brewer-Mast sondes demonstrated somewhat variable response in the troposphere, depending on preparation [*Kerr et al,* 1994; *World Climate Research Programme,* 1998; *Tarasick et al.,* 2002], recent intercomparisons show little bias in the troposphere and a precision of about 10% [*Smit and Kley,* 1998; *Stübi et al*., 2008]. The Indian sonde shows a precision of about 20% [*Smit et al.,* 1996]. The Japanese KC96 sonde shows a precision of about 5%, but a low bias in the troposphere of about 5% [*Smit and Straeter,* 2004; *Fujimoto et al.,* 2004; *Deshler et al.,* 2008]. Table 3.3 summarizes intercomparison results for the three major sonde types in current use.

Sonde Type	ECC SPC-6A SST1.0			ECC ENSCI-Z SST0.5			BM MOHp			KC96 JMA		
Altitude Range [km]	Bias [%]	Precision [%]	Accuracy [%]	Bias[%]	Precision [%]	Accuracy [%]	Bias [%]	Precision [%]	Accuracy [%]	Bias [%]	Precision [%]	Accuracy [%]
30-35	2	7	9	6	6	12	-2	13	15	11	7	18
25-30	4	5	9	7	5	12	0	5	5	5	6	11
20-25	1	5	6	5	5	10	0	5	5	-2	6	8
15-20	1	5	6	2	3	5	-1	3	4	-7	5	12
10-15	-2	4	6	-1	3	4	-3	5	8	-6	5	11
5-10	0	4	4	-1	4	5	-3	8	11	-2	4	6
0-5	-3	4	7	-1	4	5	-3	10	13	-7	6	13

Table 3-3: Survey of the average relative bias to UV-Photometer and relative precision of ECC-sonde types SPC-6A (operated with SST1.0: 1.0%KI&full buffer) and ENSCI-Z (operated with SST0.5: 0.5%KI and half buffer), BM-sonde operated by Meteorological Observatory Hohenpeissenberg (MOHp) and KC96-sonde operated by Japan Meteorological agency (JMA). The listed data are averaged over altitude bins of 5 km. The accuracy is determined as the sum of bias and precision. Results are representative for mid-latitude atmospheric conditions and are derived from SPARC-IOC-GAW [1998], JOSIE [*Smit et al.*, 2007] and BESOS [*Deshler et al.*, 2008] experiments

4. ASSESSMENT OF STANDARD OPERATING PROCEDURES FOR OZONESONDES

4.1 Introduction

Since 1996, activities to improve the quality of balloon-ozone-soundings have been conducted at the World Calibration Center for Ozonesondes (WCCOS) at FZ Juelich. In this scope, several JOSIE (Juelich Ozonesonde Intercomparison Experiment: http://www.fz-juelich.de/iek/iek-8/EN/Expertise/Infrastructure/JOSIE/JOSIE_node.html sonde simulation experiments were conducted in the laboratory to evaluate the performance of ozonesondes (Figure 4-1 left panel). The results of JOSIE clearly demonstrated that caution has to be exercised in making changes in instruments or preparation/operational procedures, as these can significantly affect sonde performance and hence ozone trends. This appeared most evident for new developments of the ECC-sonde in the mid 1990's after a new manufacturer (ENSCI-Corporation) introduced the ENSCI-Z type of ECC-sonde (Table 2-1) and ECC-sounding stations were using different sensing solution strengths (Table 2.2). JOSIE 2000 and BESOS showed the systematic differences in ozonesonde readings when using different combinations of ECC-sonde types and sensing solution strengths.

Alerted through these JOSIE 2000 results, the Assessment of Standard Operating Procedures for Ozonesondes (ASOPOS) was initiated to define easy-to-follow operating procedures that can be consistently implemented and will provide data of high quality that are comparable between ozone sounding stations. Major tasks of the assessment are: (i) to identify and evaluate major existing operating procedures and their impact on sonde data quality and (ii) establish SOPs for each of the three major sonde types.

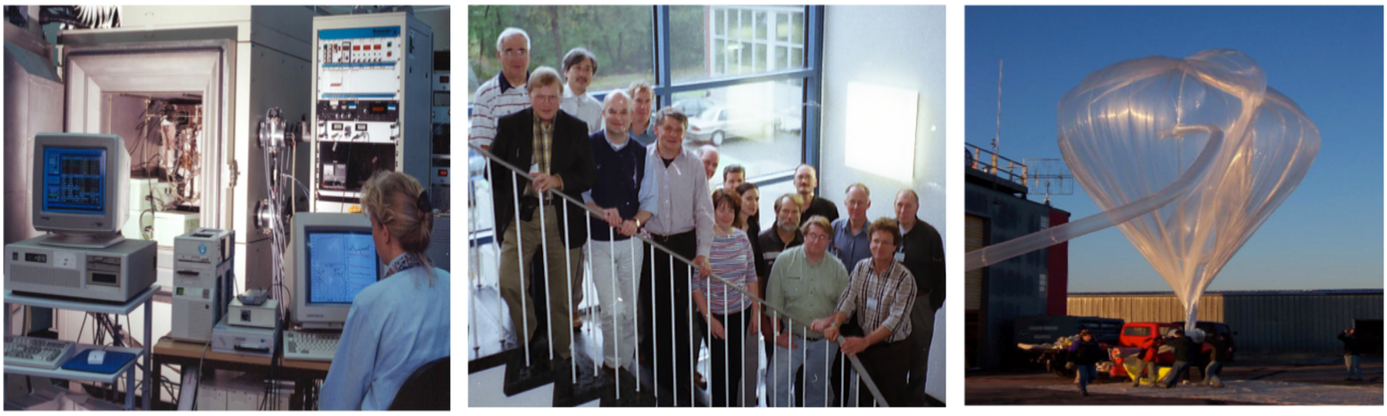

Figure 4-1: Left: JOSIE at ozonesonde simulation facility (WCCOS) at Juelich, Germany; Middle: ASOPOS-panel at ozonesonde experts meeting at September 2004, Right: BESOS field campaign at Laramie, USA, at April 2004

ASOPOS focused thereby primarily on the performance of ECC-sondes and the controversies about: the solution strength to use (SST1.0, SST0.5, or SST2.0), how to handle the decrease in pump efficiency at low pressures, which background current to use, and whether slight differences in instrument preparation and initial exposure to ozone affect the measurements significantly.

The assessment started with the WMO meeting of ozonesonde experts held in Geneva on 1-3 May 2001 to critically examine the JOSIE 1996-2000 results and to evaluate the entire JOSIE series of experiments. At this meeting, provisional SOP's (Standard Operating Procedures) were defined by the panel of ozonesonde experts. In April 2004, the WMO/BESOS (Balloon Experiment on Standards for Ozonesondes) field campaign at the University of Wyoming at Laramie, USA, was held to test the reliability of JOSIE-results in the real atmosphere (Figure 4-1 right panel).

A second WMO meeting of ozonesonde experts was held in Juelich, Germany on 20-23 September 2004 where BESOS-results were evaluated together with JOSIE and other laboratory and field studies in order to finally establish WMO-recommended SOP's, for the different major types of ozonesondes used in the GAW-ozone sounding. Final Standard Operating Procedures (SOPs) for ECC ozonesondes up to 30 km for the two manufacturers (Science Pump Corp. and EN-SCI Corp.) were unanimously agreed upon by the assessment panel (Figure 4-1 middle panel).

This chapter contains the major conclusions and recommendations made by ASOPOS with regard to standard operating procedures for ozonesondes. In this context, the major results of JOSIE and BESOS are briefly presented and discussed. In addition, the transfer from BM to ECC sonde types at two long term sounding stations (Uccle, Belgium and Payerne, Switzerland) are reported. For each sonde type (ECC, BM and KC96) a brief overview of the SOPs are given. For the ECC and BM sonde corresponding comprehensive practical guidances of SOPs are given in Annex A and B, respectively. Since 2011, the Japanese sounding network has changed from KC96 to ECC-sondes and the production of KC96 have been stopped therefore no KC96 sondes will be flown in the future.

4.2 JOSIE & BESOS Experiments

The JOSIE experiments were conducted in an environmental simulation chamber to determine precision, accuracy and response of the ozonesondes as a function of sonde type, altitude, and ozone level. The different ozonesonde types were tested under a variety of conditions and compared with an accurate ozone UV-photometer. Special attention was paid to the influence of pre-launch procedures on in-flight performance. In addition, the influence of certain procedures, such as background signal correction and total ozone column normalization, was investigated. The JOSIE 1996-2000 experiments, their design and results are presented in detail in three GAW reports [*Smit and Kley*, 1996 and *Smit and Straeter,* 2004a & 2004b) and evaluated in peer reviewed literature by *Smit et al.* [2007]. In 2004 during BESOS the results from JOSIE were tested in the field by a balloon flight carrying a core of 12 ECC sondes and an in-situ photometer [*Deshler et al.*, 2008].

4.2.1 JOSIE 1996

Josie 1996 was designed to assess the performance of the major ozonesonde types (ECC, BM and KC79) and was attended by representatives of eight laboratories involved in the GAW ozonesonde network. The focus was on assessing whether differences in instrument preparation and data analysis from each laboratory would cause significant differences in the measurements. Figure 4-2 shows a summary of JOSIE 1996.

JOSIE showed that ECC-type sondes can achieve a precision within ±(3-4)% and an accuracy of about ±(4-5)% in the troposphere and lower/middle stratosphere up to 30-35 km altitude. The different performance characteristics of the ECC-sondes (CMDL [2] and CNRS [7]) was caused by different operating procedures. Non-ECC type sondes exhibited in general higher variability and larger deviations from the UV-photometer measurements than the ECC sondes. The behaviour of the different non-ECC-sonde types is quite different. The original BM-sonde operated by Meteorological Observatory Hohenpeissenberg (MOHp) exhibited a precision of about ±(3-5) % and an accuracy of about ±5% in the stratosphere up to 30 km altitude while, in the troposphere, the precision was somewhat lower with values of about ±10 % and the accuracy was ±(10-13) %. The KC79-sonde tended to underestimate ozone in the troposphere (precision≈±6% and accuracy≈±10%) and lower stratosphere (precision ≈±5% and accuracy ≈ ±10%) and to overestimate ozone above 25 km altitude (precision≈±7% and accuracy ≈±(11-18)%). The Indian BM sonde showed a precision of about ±(4-8)% and an accuracy ±(6-13)% in the lower stratosphere, with decaying performance above 30 km altitude. In the troposphere the sonde showed strong fluctuations and deviations from the UV-photometer. The BM-Hybrid/ASP, a research type of ozonesonde flown by MeteoSuisse, gave good performance in the lower stratosphere (precision ≈ ±4% and accuracy ≈ ±5%) up to 30 km. However, in the troposphere the sonde had low precision (≈ ±18%) and low accuracy (≈ ±33%).

Although all individual normalization factors ranged between 0.9 and 1.1, the variability (standard deviation) of the ECC-sonde types with values of ± 0.02 for three of the four ECC-stations is significantly smaller than the variability of the other types of sondes, at values of ±(0.07-0.10). The normalization factors for the non-ECC-type sondes are closer to unity than usually achieved during field operations at the sounding site (Figure 3-3).

The observed larger variability among ozonesonde measurements in the middle stratosphere is mainly caused by uncertainties in the pump efficiency and by the amount of evaporating sensing solution. Significant differences (more than 5-10 % at 5 hPa) were observed between the various experimental methods used to determine the pump flow efficiency at lower pressures. JOSIE indicated that it is most likely that the conversion efficiency, i.e. the sensitivity of the ECC-sonde increases during flight due to evaporation caused changes of the concentrations of the sensing solutions [*Smit et al.,* 2007].

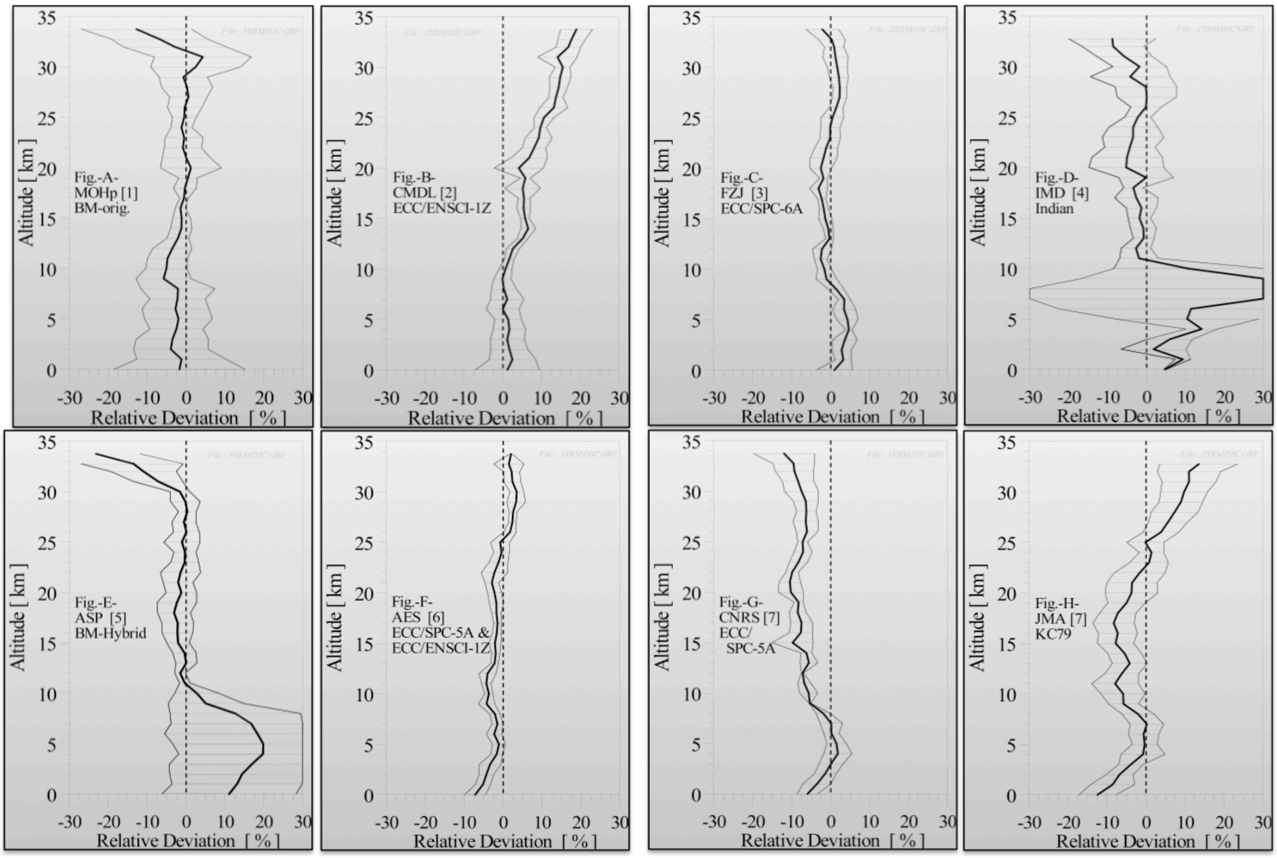

Figure 4-2: JOSIE-1996: Average (thick line) plus/minus one standard deviation (thin lines) of the relative deviations of the individual sonde readings from the UV-photometer for each participating sounding laboratory obtained from six simulation runs. All ECC sondes were operated with SST1.0 sensing solution. Data shown from sondes operated by MOHp [1], IMD [4], ASP [5], AES [6] and JMA [8] are normalized to the photometer ozone column [*Smit and Kley,* 1998]

4.2.2 JOSIE 1998

Josie 1998 focused on a quality check of the instrumental performance of newly manufactured ECC-sondes. Twenty-six ECC-sondes, 13 sondes of each model type (SPC-6A and ENSCI-Z), randomly picked from stocks at different sounding sites, were tested where all sondes were operated with SST1.0 sensing solution (Figure 4-3). All sondes were processed according to Komhyr [1986]: use of (i) external pump temperature; (ii) pressure dependent background current correction (IB3, measured just prior to launch); (iii) pump flow correction at low pressures for SPC-6A *Komhyr* [1986] and ENSCI-Z *Komhyr et al*.[1995] (Table 3.1), (iv) No total ozone normalization.

In the troposphere and lower stratosphere up to 20 km altitude both sonde types have a rather similar performance. Below 20 km altitude a precision of ±(3-4)% has been consistently observed while both sonde types tend to overestimate ozone by about 5-10 %, particularly in the troposphere. In the stratosphere above 20 km altitude, the sonde types start to deviate from each other quite significantly. The precision of the SPC-6A sonde decreases with altitude to about ±(5-10)% while the observed bias changes sign with altitude from about +5% at 25 km to -8% at 35 km. This is in contrast to the ENSCI-Z sonde type that exhibits a precision of ±(4-5)% and a rather large positive bias of about 10% up to 35 km altitude. Shortly after the JOSIE 1996 campaign the ENSCI-manufacturer recommended the use of 0.5% KI, half pH buffered sensing solution for the ENSCI-Z sonde [*ENSCI-Corporation,* 1996], which would lower the ozone readings by about 5% [*Johnson et al*., 2002].

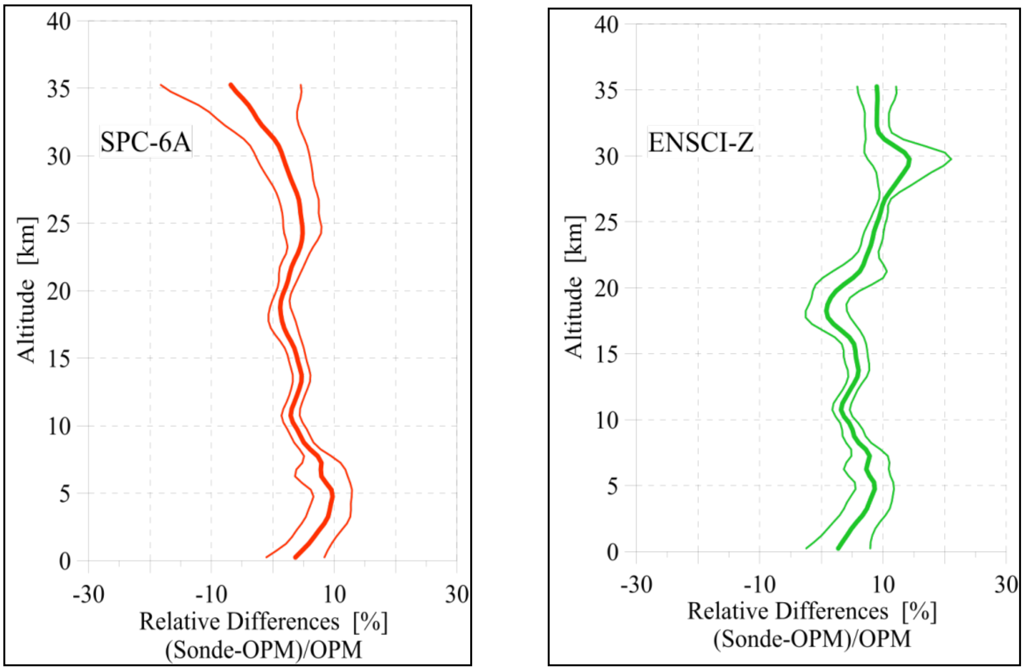

Figure 4-3: JOSIE-1998: Comparison of 13 tested ENSCI-Z (A) and 13 tested SPC-6A (B) ozonesondes. Results presented as averaged (± 1 σ) relative deviations of the individual sonde readings from the UV-photometer (OPM). All sondes were prepared (including use of SST1.0) and data were processed according to Komhyr [1986]: use of (i) external pump temperature; (ii) pressure dependent background current correction (IB1, measured before exposure with ozone); (iii) pump flow correction at low pressures for SPC-6A and ENSCI-Z *Komhyr*.[1986] (Table 3.1), (iv) No total ozone normalization.

JOSIE-1998 showed clearly that the performance characteristics of the two ECC-sonde types are significantly different in the middle stratosphere above 25 km, when using the same sensing solution strength. The origin of the observed differences is not really understood. Large sources of uncertainty exist with regard to the corrections applied for the degrading pump efficiency at lower pressures or the choice of the chemical composition of the sensing solution in the cathode cell [*Johnson et al.,* 2002].

4.2.3 JOSIE 2000

JOSIE 2000 investigated the influence of the use of three different cathode sensing solutions (SST1.0: 1.0% potassium iodide (KI) & full buffer strength; SST0.5: 0.5% KI & half buffer strength; SST2.9: 2.0% KI & unbuffered) on the performance of both ECC-sonde types. JOSIE 2000 brought together 7 sounding stations testing ECC-sondes (SPC-6A & ENSCI-Z) with the three different solution types (Table 2-2). Each sounding laboratory participated in six simulation experiments. For each SST a similar number of SPC-6A sondes and ENSCI-Z sondes were tested. The pre-launch procedures of each ozonesonde prior to a run were performed by the field operators of the participating stations using their own ground test equipment. All ECC-sonde data were processed and corrected according to the operating procedures of *Komhyr* [1986].

For each combination of sonde type and SST, the overall sonde comparisons with the UV-photometer are displayed as relative deviations from the UV-photometer in Figures 4-4. Throughout the entire ozone profile systematic features of the different SST are seen by comparing the performance of ENSCI-Z and SPC-6A sondes. For both sonde types there is a systematic change in the ozonesonde readings of about 5-15% with differing SST. A change from SST1.0 to SST0.5 or from SST0.5 to SST2.0 produces a change in the ozone reading up to 5-10%, depending on the altitude. A maximum ozone difference of more than 10% can be expected when changing from SST1.0 to SST2.0.

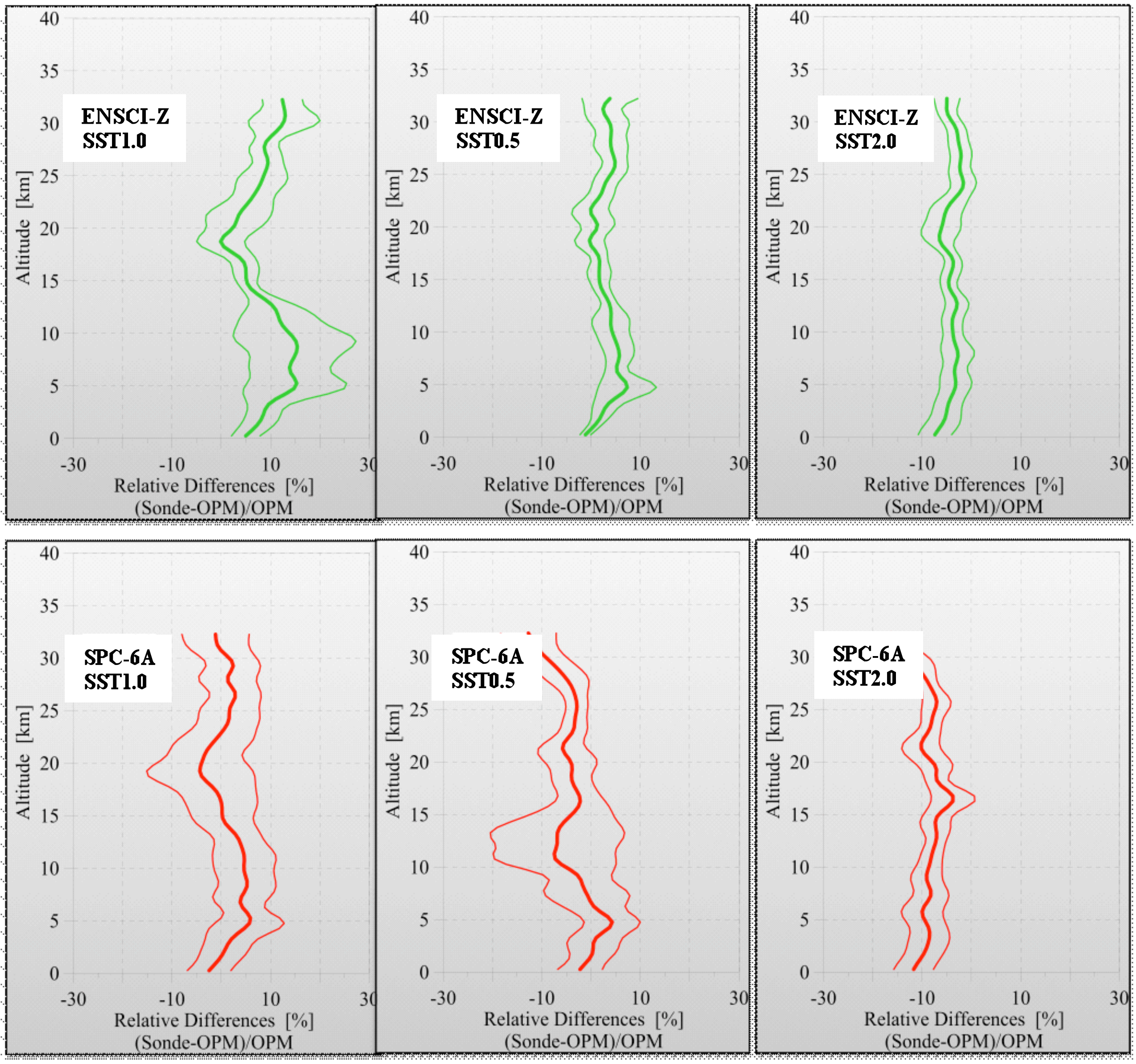

Figure 4-4: JOSIE 2000: Overview of the comparison of the two different ECC-sonde types (SPC-6A and ENSCI-Z) with a UV-photometer. Both ECC-sonde types were operated with three different sensing solutions. Presented are the averages (± one standard deviation) of the individual sonde readings of each ensemble of sondes. All sondes were prepared and data were processed according to Komhyr [1986]: use of (i) external pump temperature; (ii) pressure dependent background current correction (IB1, measured before exposure with ozone); (iii) pump flow correction at low pressures for SPC-6A and ENSCI-Z *Komhyr*.[1986] table (Table 3.1), (iv) No total ozone normalization.

Both sonde types show a relative variability i.e. precision of about ±(3-6) % throughout the entire profile with some outliers up to ~±12 %. The origin of these outliers is not really understood. Although, also good precision for both sonde types is achieved with SST2.0, they exhibited a significant negative bias with values of –(7-15)% for SPC-6A and –(3-8)% for ENSCI-Z sondes depending on altitude. The least biased results are achieved for SPC-6A sondes with SST1.0 and ENSCI-Z sondes with SST0.5. For both sonde types the bias relative to the UV-photometer is less than 5% and the relative differences between both sonde types is only 2-5% at all altitudes. A more detailed evaluation of the JOSIE results are published by *Smit et al.* [*2007*].

Based on these results ASOPOS defined provisional SOPs for ECC-sondes (See Section 4-5) and the ASOPOS-panel agreed unanimously to recommend for the GAW ozone sounding network to fly SPC-6A with SST1.0 and ENSCIZ with SST0.5.

4.2.4 BESOS

To test the provisional SOPs a balloon flight carrying a core of 12 ECC ozonesondes from two manufacturers prepared with the use of cathode solution concentrations of SST0.5 and SST1.0 was completed in April 2004. The experiment tested the consistency of groups of ozonesondes, prepared similarly, and their accuracy in comparison with an ozone photometer (Figure 4-5). This was the same photometer as used in the JOSIE chamber experiments, but modified for balloon-borne flight.

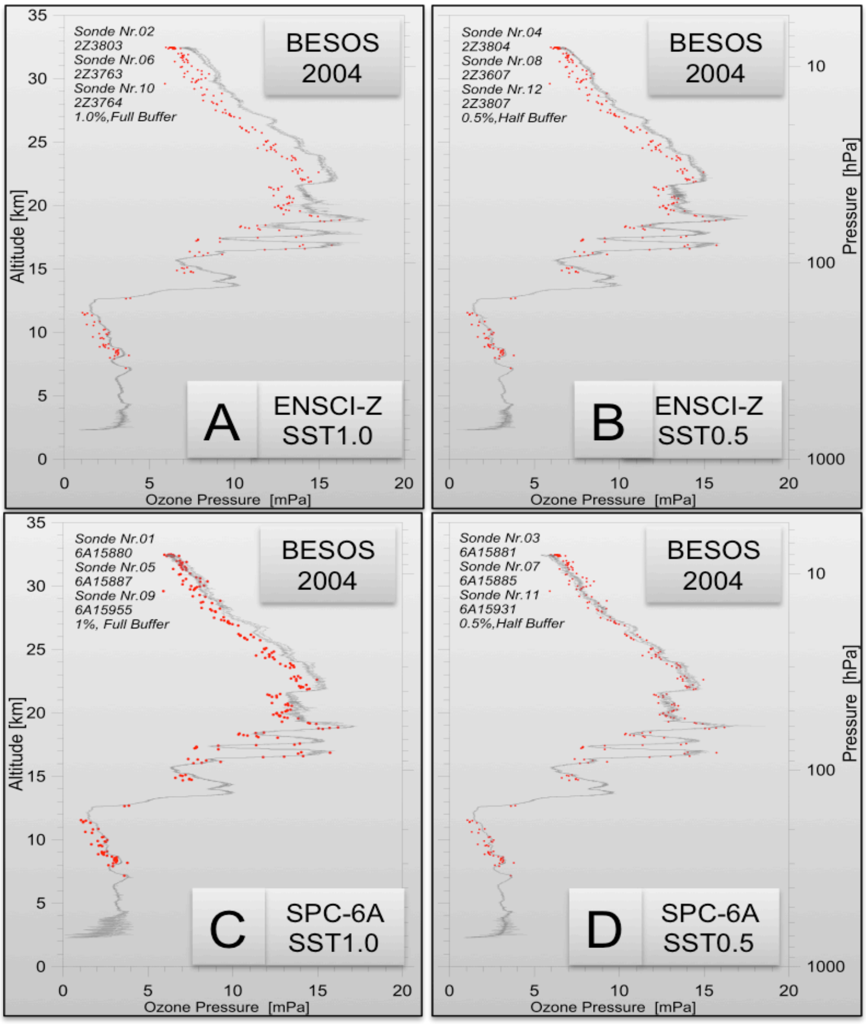

Figure 4-5: BESOS: Ozone profiles (grey curves) obtained from each of the four groups of three sondes: ENSCI-Z/SST1.0 (A), ENSCI-Z/SST0.5 (B), SPC-6A/SST1.0 (C) , SPC-6A/SST0.5 (D). Red solid dots represent ozone measurement made with UV-photometer. All sondes processed according to provisional SOPs: use of (i) internal pump temperature; (ii) full background current correction (IB3), measured just prior to launch); (iii) pump flow correction at low pressures for SPC-6A *Komhyr* [1986] and ENSCI-Z *Komhyr et al.*[1995] (Table 3.1), (iv) No total ozone normalization

The 12 core ozonesondes showed a high precision within each group of three sondes [See Figure 4.5]. In general the precision was better than 2% except in regions where ozone is low, near the surface and just below the tropopause, or where ozone gradients are high, such as between 50 and 100 hPa [*Deshler et al.*, 2008]. In these locations the precision decreased to 4-5%. Similar to the experience made during JOSIE 1998 it is obvious that when using exactly the same operating procedures and same equipment for preparation a very good precision within a few percent can be achieved throughout the entire vertical profile.

While the ozonesondes performed very well, unfortunately the UV-photometer performance suffered from UV-lamp instabilities. Although these lamp instabilities were not seen during JOSIE nor during BESOS preflight and post flight checks, they were present during much of the BESOS flight. The photometer problems arose most likely due to swinging and rotating of the gondola in the Earth's magnetic field affecting the plasma lamp of the photometer. The analysis of these data to remove this effect required careful examination of the measurements to isolate periods when lamp instabilities were at a minimum. Only a limited fraction of data could be recovered and first quasi continuous measurements are only available above 10 km. While in JOSIE the photometer accuracy was better than ±(3-5)% [*Smit et al.*, 2007] during BESOS only a reduced accuracy of about ±(5-7)% [*Deshler et al.*, 2008] could be achieved. Comparing total ozone column estimated from the photometer with column measurements made with remote spectrometers (a Dobson and a Brewer) indicated that the in-situ photometer might have underestimated ozone by 3-5 % [*Deshler et al.,* 2008]. A direct justification for such a shift of the photometer measurements is not available, and post flight tests are not illuminating. The arguments in favour of such a shift are the poor flight performance, the internal consistency of all BESOS sonde data with all JOSIE data and with the remote column measurements [*Deshler et al.*, 2008].

The comparisons of the twelve core ozonesondes with the in situ UV-photometer measurements are shown in Figure 4-6 for altitudes above 18 km, i.e. pressures less than 70 hPa. There were not enough photometer measurements below this altitude from the balloon flight to warrant a comparison and thus assessments of the accuracy of the tropospheric ozonesonde data. Corresponding JOSIE 2000 results are included. Figure 4-6 indicates that in the stratosphere the JOSIE 2000 and BESOS results are quite consistent for each sonde type and solution strength combination. The JOSIE 2000 measurements for all the SPC-6A and ENSCI-Z variations lie within about 2-5 % at the lower boundary of the BESOS measurements. A similar shift was observed comparing total ozone column estimated from the photometer with column measurements made with spectrometers. For a more detailed evaluation of the BESOS results see in *Deshler et al.* [2008].

The JOSIE & BESOS experiments all indicated that, when operated under similar conditions, following the same guidelines and using the same sensing solution strength ENSCI-Z sondes measure more ozone than SPC-6A sondes (Figure 4-7). In the middle stratosphere above 25 km altitude the ENSCI-Z-sonde measures 5-10% more ozone than the SPC-6A sonde. Below 25 km the differences between both sonde types and the UV-photometer were less than 5% during JOSIE 1998 but were 10-15% during JOSIE 2000.

JOSIE 2000 and BESOS have clearly shown that independent of the SST, the performance characteristics of the ENSCI-Z and SPC-6A sondes are different (Figure 4-7). The relative differences between both sonde types as a function of altitude are very similar for SST1.0, and SST0.5. When both sonde types are operated with the same SST they exhibit systematic differences of ~5% in the stratosphere and 5-10% in the troposphere which can vary from campaign to campaign. The origin of these differences is not known at the present. Above 25-30 km altitude the differences increase up to 10-15%. Good results are achieved for SPC-6A sondes with SST1.0 and ENSCI-Z sondes with SST0.5. Both sonde types exhibit a bias relative to the UV-photometer less than 5 % and (Figure 4-6) and the lowest relative differences between both sonde types with values of 2-5% at all altitudes (Figure 4-7). These combinations match the manufacturer recommendations on the use of sensing solution type.

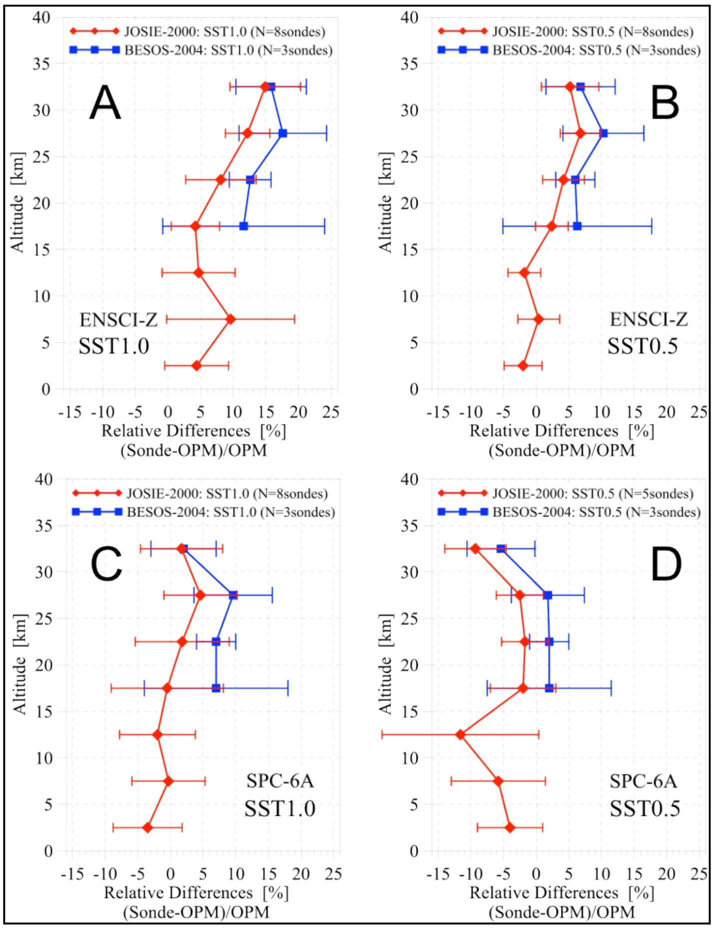

Figure 4-6: JOSIE 2000 (red curves) & BESOS (blue curves): Average (±1σ-uncertainty bars) of the relative deviations of the individual sonde readings from the UV-photometer for each group of three sondes: ENSCI-Z/SST1.0 (A) ; ENSCI-Z/SST0.5 (B) ; SPC-6A/SST1.0 (C) ; SPC-6A/SST0.5 (D). Note: JOSIE 2000 results have been corrected for differences occurring between the use of external pump temperature in JOSIE and internal pump temperature in BESOS (Section 3.2.5, Figure 3-3). Data are averaged over 5 km altitude bins

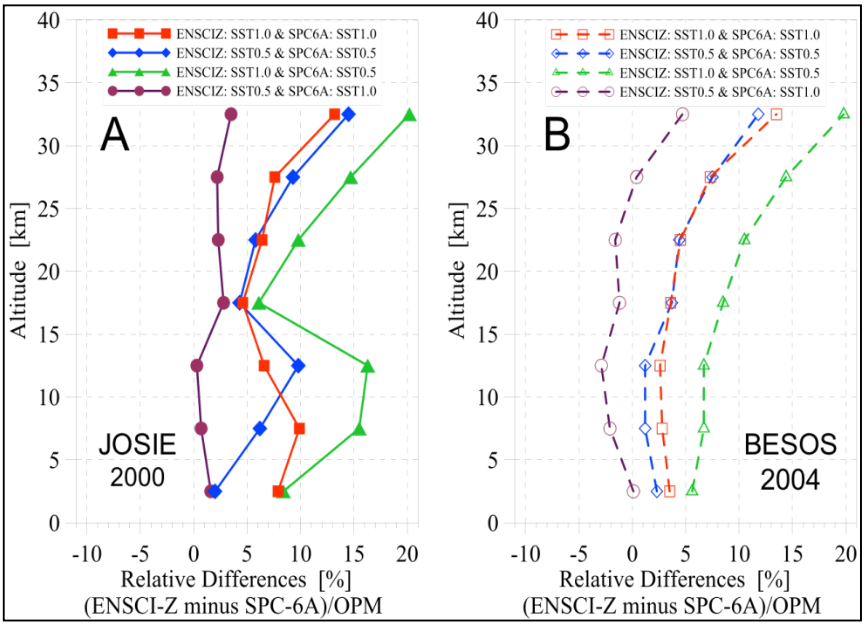

Figure 4-7: JOSIE 2000 (A) & BESOS (B): Relative differences between ENSCI-Z and SPC-6A sondes in case of different combinations of SST1.0 and SST0.5 sensing solution strength. Data are averaged over 5 km altitude bins

4.3 Change over from Brewer-Mast (BM) to ECC ozonesonde type

A change over from one type of ozone sensor to another can influence the long-term ozone sounding record of a station. The change has to be carried out very carefully in order to avoid risks of generating artifacts in the long term trends derived from the sounding record of the station. Uccle and Payerne, two well established long term sounding stations that flew BM-sondes since late 1960's, have changed to ECC-sondes during last decade. This has been achieved at both stations by conducting a large number of dual soundings of both ozone sensor types over a period of several months to years.

4.3.1 Homogenisation of BM and Z-ECC sonde ozone profiles at Uccle

At Uccle a change from Brewer-Mast (BM) to Z-ECC (from EN-SCI corp.) took place in April 1997. Before and after the transition a number of dual soundings were performed. Analyses of this data set, together with investigations in a vacuum chamber, gave rise to a new method to correct the ozone profiles for the decreasing pump efficiency with altitude [*De Backer et al.,* 1998].

The method is based on a single point calibration of the individual sensors in the laboratory at ambient pressure and the measurement of the total ozone column with a spectrophotometer. Also the change in the pump efficiency with the temperature inside the ozone box is considered. The same principle is applied both to ECC and BM sondes. A description of the procedure can be found in *De Backer et al.* [1998]. The application to construct a homogenous time series is documented by *De Backer* [1999]. Figure 4-8 shows the relative differences between BM and Z-ECC profiles obtained from 27 dual soundings applying the different normalisation procedures for total ozone column. It can be seen that the standard normalisation by linear scaling of the vertical ozone profile [*Claude et al.,* 1986 for BM and *EN-SCI Corporation,* 1996 for Z-ECC] overestimates tropospheric ozone from the BM by about 10%, while stratospheric ozone is underestimated, depending on altitude from 2% at 50 hPa to more than 5 % at 10hPa. The application of the height dependent pump correction reduces the differences to about 2 % over almost the whole altitude range.

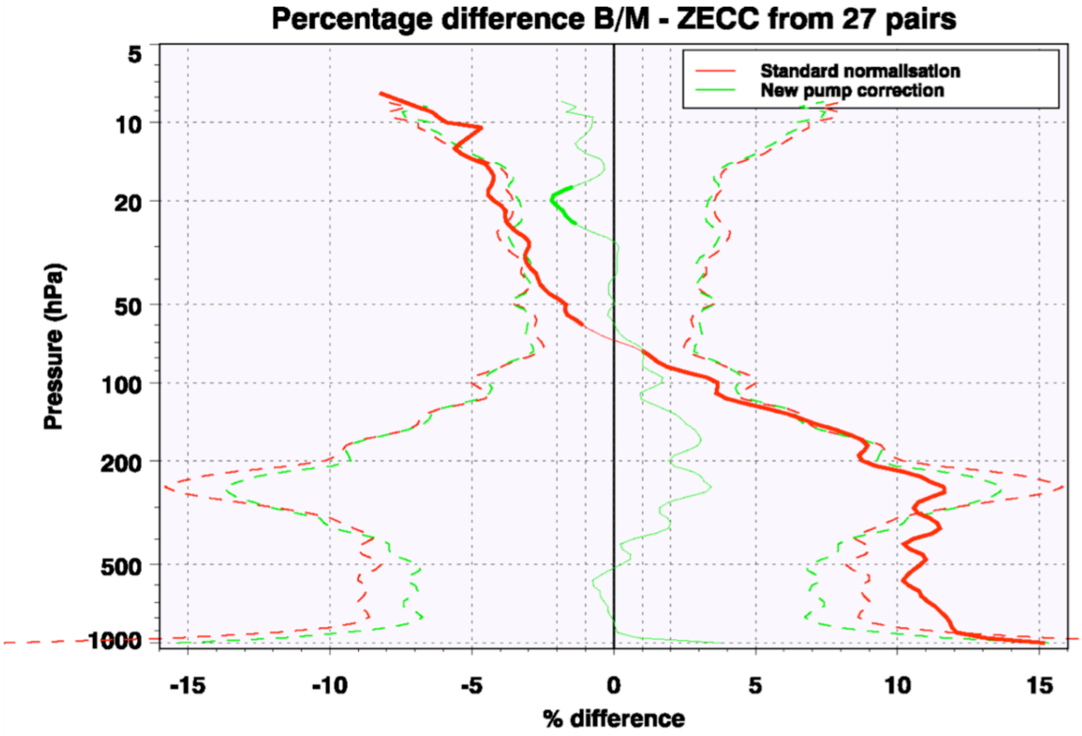

Figure 4-8: Mean percentage difference between ozone profiles obtained from measurements with BM and Z-ECC sondes with standard (red) and the new pump (green) corrections in Uccle. The domains where the differences are statistically significant at the 95% confidence limit according to a 2-tailed student-t test are indicated by thick segments of the lines. The dashed lines give the 1-sigma levels of the differences

The procedure was further validated by comparison of the sonde data with SAGE II ozone profiles [*Lemoine and De Backer,* 2001]. They show that for the period 1985-1997 in the altitude range 17 - 22 km, the relative drift between sondes and satellite which amounted to –0.51%/year with the standard corrections is reduced to a non-significant –0.07%/year with the new procedure.

4.3.2 Transition of BM to Z-ECC sondes at Payerne

Different campaigns of dual flights of BM- and ECC-sondes have been conducted at Payerne over the period 1996 to 2002 in preparation to the change from BM-to ECC-sonde for the operational service. A record of 140 valid flights has been analysed to evaluate the systematic differences that appear between both sonde types. The influence of the data processing algorithm for both sonde types has been evaluated to quantify the sensitivity of the ozone profile retrieval toward different parameters [*Stuebi et al*., 2008]. The ECC sondes were from EN-SCI Corp, and the sensing solution was a 1% KI, fully buffered [*Komhyr,* 1986]. The background current, which was measured 40 minutes after switching off from ~20 mPa to zero ozone, is assumed constant during the entire flight. The pump temperature is measured inside the pump body and the pump efficiency correction table is after *Komhyr* [1986]. BM sondes are from the Mast-Keystone Corp. and they have been handled according to the SOP defined for those sondes. In the data processing algorithm, the back-ground current is set to 0, the pump temperature is constant (Tp=280 K) and the pump efficiency is from Komhyr (1969). All ozonesonde profiles have been normalized (c.q. linearly scaled) toward an independent total ozone column measurement.

The results of a total of 111 BM/ECC-intercomparison flights are summarized in Figure 4-9. Good agreement between the two ozonesonde types under the specific conditions (preparation procedures, data processing, etc.) prevailing during these intercomparion flights was obtained [*Stuebi et al*., 2008]. The seasonal mean of ozone differences (BM-ECC) show that between the surface and 25 km altitude the observed ozone pressure differences are within the range of ±(0.2-0.4) mPa. A small positive bias of (0-0.2) mPa for BM compared to ECC is observed that corresponds to about +(0-5)% in the troposphere and +(0-2%) in the stratosphere. Above 25 km altitude BM-sondes show reading lower ozone values than ECC-sondes. No seasonal dependence was observed. Although, slight altitude dependence is seen in the seasonal profiles, the differences are generally not significant at the 90% confidence level (see error bars on the left panel) and therefore no detectable differences were expected in the Payerne time series at the change from BM- to ECC-sondes.

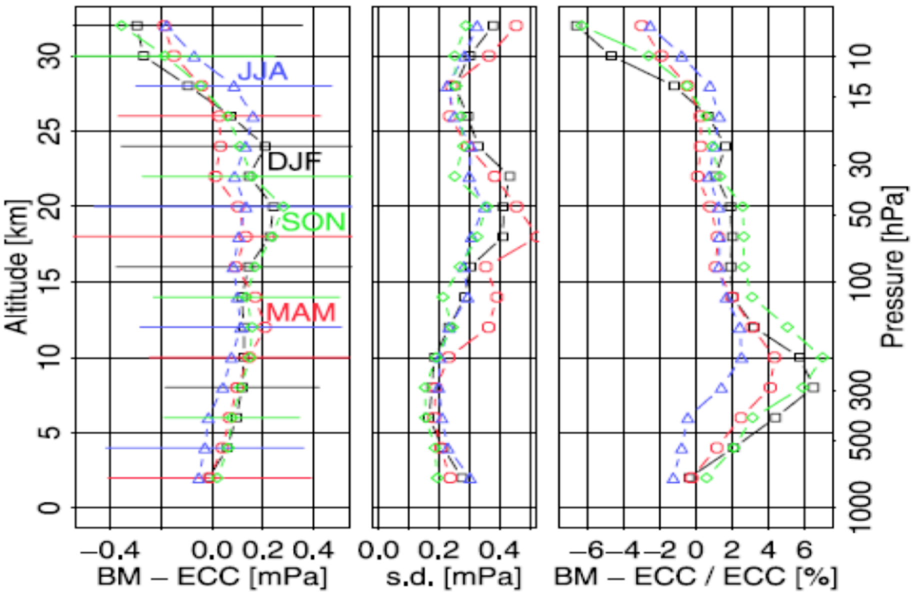

Figure 4-9: Mean ozone difference (BM-ECC) as function of altitude at four seasons seasons: DJF (squares), MAM (circles), JJA (triangles), and SON (diamonds) obtained from 111 dual soundings of BM-and ECC- (EN-SCI) sonde types made between 1996 and 2002

4.4 Improvements of KC79/K96 ozonesondes: AKC 2004-algorithm

Results of simulation chamber experiment JOSIE and field experiment BESOS showed that derived ozone profiles by KC79/96 ozonesondes tend to measure lower values in the lower atmosphere and higher values in the upper atmosphere when referred to UV ozone photometer [*Smit and Straeter*, 2004; *Deshler et al*., 2008] (See Figure 4-10-A). Laboratory experiments leaded to new insights in KC96-sonde data processing [*Fujimoto et al.*, 2004]:

(a) Measured cell current is dependent on sensing solution temperature. Theoretically, one molecule ozone causes a flow of two electrons in the circuit, but actually the current flow is larger than expected. This excessive current that is dependent on sensing solution temperature has been experimentally characterized in the laboratory, and an algorithm has been derived to correct for this sensing solution temperature effect.

(b) Delay effect on measured cell current due to relatively long response time of 40 s. Based on laboratory response experiments at different cell temperatures an algorithm has been developed to correct for the delay effect (incl. dependence of the solution temperature).

(c) Background current is dependent on ozone exposure and sensing solution temperature. The observed background current reveals to be related to slow decomposition of unknown chemical byproducts generated during ozone reaction in the solution. The rate of decomposition is dependent on the solution temperature. Based on laboratory experiments the background current corrections is derived as function of ozone exposure and solution temperature.

(d) A new pump efficiency C_{PF} as a function of air pressure have been determined experimentally.

Based on these new insights a new data processing algorithm (AKC-2004 algorithm) has been developed that is described in more detail by *Fujimoto et al.* [2004]. By using the AKC-2004 algorithm the deduced ozone profile is qualitatively improved when referred to UV photometer (*Fujimoto et al.,* 2004) as demonstrated in Figure. 4-10. JMA is preparing to use the AKC-2004 algorithm operationally and consequently to revise all the past KC79/96 ozonesonde data using the new algorithm.

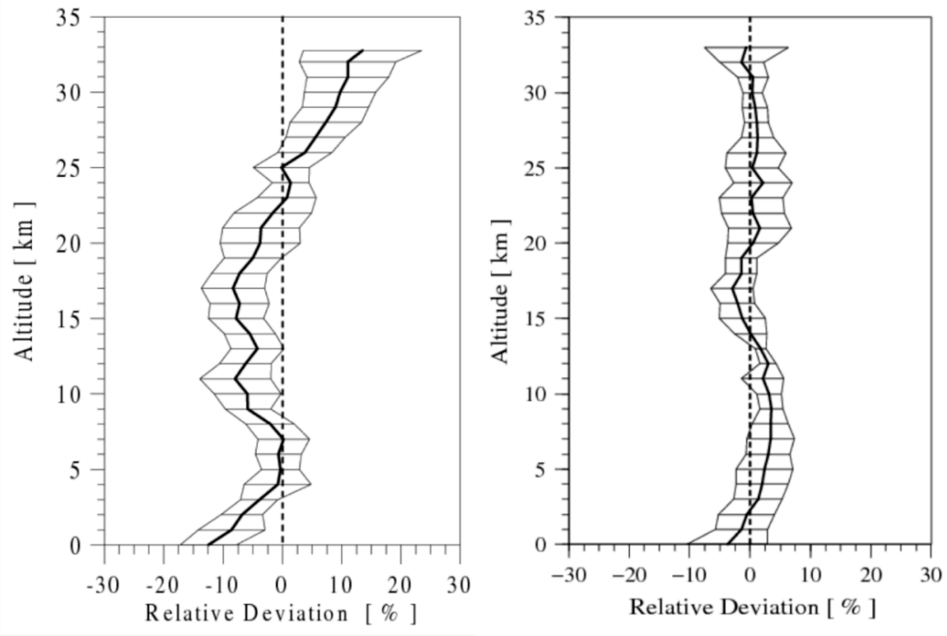

Figure 4-10: Relative deviations of ozone concentration by KC ozonesonde referred to UV photometer derived by traditional algorithm (A) and AKC-2004 algorithm (B) [*Fujimoto et al.*, 2004]

4.5 Major Conclusions and Recommendations by ASOPOS

4.5.1 Standard Operating Procedures (SOP's)

After a critical evaluation of the entire series of JOSIE and BESOS experiments unanimous agreement on SOP's for ECC-sondes was achieved by the ASOPOS-panel (See Annex C) in September 2004 at the WMO/ASOPOS meeting held in Juelich, Germany. The panel has concluded that the performance characteristics of the two ECC-sonde types can be significantly different, even when operated under the same conditions. There is a significant difference in the ozone readings when ECC-sondes of the same type are operated with different cathode sensing solutions. Testing the most commonly used sensing solutions showed that for each ECC manufacturer type the use of 1.0% KI and full buffer gives 5% larger ozone values compared with the use of 0.5% KI and half buffer, and as much as 10% larger values compared with 2.0% KI and no buffer. SPC-6A sondes with SST1.0 and ENSCI-Z sondes with SST0.5 exhibit the smallest bias relative to the UVphotometer, less than 5%, while the relative differences between both sonde types is only 2–5% at all altitudes.

ASOPOS recommends on the use of sensing solution the following:

- **SPC6A: 1.0% KI, full buffer (SST1.0)**
- **ENSCI : 0.5% KI, half buffer (SST0.5)**

Important thereby is that the recommendation is exclusively meant for new ozone sounding stations. The existing stations that perform long term measurements should not change their sensing solution type or ECC-sonde type

Any change of sonde type or SST this would introduce discontinuities of ±5% or more in their records, affecting the determination of ozone trends significantly. The combinations of EEC-type with SST as recommended by ASOPOS match the manufacturer recommendations on the use of sensing solution type.

ASOPOS has formulated and reviewed standard operating procedures for ECC-sondes (See Section 4.6), which have been approved by the Scientific Advisory Group for Ozone (SAG-O3) of the WMO/GAW at the annual SAG-O3 meeting at Tenerife in April 2007.

Standardization of the operating procedures (SOP's) leads to the best precision and accuracy (<±5 %). The sonde to sonde differences observed in JOSIE are borne out in BESOS such that the JOSIE-simulation chamber experiments are representative for the real atmosphere, sonde to sonde and in comparison with a UV-photometer as an ozone reference instrument. JOSIE and BESOS demonstrated that small changes of an ozonesonde instrument (e.g. different manufacturers) or operating procedures (e.g. different sensing solutions) can have a large impact on sonde data quality. Together with nonuniformity in data processing this can lead to large inhomogenities in time series and records between stations caused by changes of instrument or operating procedures and thus may influence the trends derived from such records dramatically. ASOPOS demonstrated that after standardization and homogenization improvement of precision and accuracy by about factor 2 might be yielded.

4.5.2 Re-use of Recovered Sondes

ASOPOS panel concluded that at present it is not clear in how far recovered ozonesondes can be re-used after reconditioning. For ECC-sondes no guarantees can be given on re-used sondes, some are good, others not. Therefore, the general recommendation by ASOPOS-panel is not to fly re-used ECC-sondes. Despite, if individual sounding stations decide to deploy re-used sondes, the reconditioning of the recovered sondes should be done by well skilled and trained personal. Even in spite of great care the station do it on their own risk and should be aware that they easily can introduce artifacts in their long term ozone records. The procedures of reconditioning recovered ozonesondes as given by the manufacturers has to be taken with great care, particularly with respect to any disassembling or adjustments of the Teflon gas sampling pump.

4.5.3 Future Activities of WCCOS

For future (5-10 year) activities the ASOPOS-panel strongly recommend that the WCCOS should focus on:

1. Implementation of SOP's in the global network. Deriving transfer functions for non-SOP data to facilitate homogenization of sonde data. This has been partly achieved through the JOSIE and BESOS experiments and can be pursued further through intercomparison experiments in the simulation chamber at the WCCOS and in the field.
2. QA-Manufacturing of sondes on a regular basis (every 1-2 years): JOSIE.
3. QA-SOP by regular evaluation and eventual update (every 5 years).
4. Scientific research on outstanding issues (e.g. background signal, pump flow efficiency, total ozone normalization, increase of sonde sensitivity at lower pressures in the stratosphere).

To assist in the implementation of standard operation procedures in the global ozone sounding network and quality-control methodologies for ozonesonde profiles an International Expert Workshop on Ozonesondes was held in February 2009 at Juelich with the goal to set up a strategy (incl. recommendations and action plans) for future research on: (i) instrumental performance of ozonesondes and (ii) empirical transfer functions to homogenize discontinuities of sounding data records.

Four important outstanding instrumental issues for O_3 sondes were identified (in order of priority):

1. The correction for the background current can have a significant impact on tropospheric values. However, the origin is very poorly understood and more fundamental research is needed.
2. Pump flow correction factor: there is a variety of different experimental methods to determine the pump flow rate at low pressures, showing significant but unexplained differences, which should be experimentally evaluated.
3. Chemical kinetics (Stoichiometry of O_3 into I_2): Quantifying the observed increase of sensitivity of ozonesondes at low pressures. What is the origin of this result? How should it be accounted for in data analysis.
4. Reconsidering the use of total ozone correction (normalization) factor for troposphere, stratosphere up to Z=30 km and above Z= 30 km. The benefits to use linear scaling of O_3 profile by total ozone measurements is not proven, particularly for the troposphere for which experimental evidence is lacking.

At present, ozone sounding records of different sounding stations show Inhomogenities/discontinuities through use of different:

a. Sensing techniques (e.g. ECC, BM , KC96, ….)
b. Sensor types (e.g. ECC: SPC-4A,-5A,-6A , and ENSCI-Z)
c. Sensing solutions types (e.g. ECC: SST1.0=1%KI+full buffer, SST0.5=0.5%KI+half buffer, or any other SST)
d. Radiosonde types

To resolve these artifacts sounding records have to be homogenized either in space (between different stations) or in time (long term changes) through use of empirical transfer functions which can be derived from (i) intercomparison experiments (e.g. JOSIE or BESOS); (ii) dual balloon soundings (iii) other approaches.

4.6 SOPs for ECC, BM and KC96 ozonesondes

In the following three sub-section for each sonde type (ECC, BM and KC96) a brief overview of the SOPs are given. In Annex A-1 and A-2 comprehensive practical guidances of SOPs for the ECC and BM sonde are given, respectively. Since 2011, the Japanese sounding network has changed from KC96 to ECC-sondes such that no KC96 sondes will be flown in the future and no practical guidances of SOPs for KC96 are included in Annex A [5].

4.6.1 Overview of SOPs for ECC sondes (SPC-6A and ENSCI-Z)

This Section presents a brief overview of SOP's for ECC-sondes which are based on the decisions and recommendations made by the ASOPOS panel [Annex B] at the WMO-ASOPOS meeting held in September 2004. After formulation and peer review the SOP's have been approved by the Scientific Advisory Group for Ozone (SAG-O_3) of the WMO/GAW at the annual SAG-O_3 meeting at Tenerife in April 2007.

Recommendations by ASOPOS panel:

1. Use of cathode sensing solution strength:

- SPC6A: 1.0% KI, full buffer (SST1.0)
- ENSCI: 0.5% KI, half buffer (SST0.5)

Important: At present only new ozone sounding stations should follow this recommendation. Existing sounding stations should not change ECC sonde type or sensing solution type.

2. Measurement of cell current I_M and I_B with resolution better than 0.01µA
3. Measurement of internal pump temperature $T_{P,Int}$
4. Only use of brand new sondes: **No** re-use of recovered sondes

I. Advance preparation, normally 3-7 days before flight (up to 3 weeks ok):

In the laboratory:

1. Run new ozonesonde on purified air free of ozone for 10 minutes
   - A. Check pump motor current (must be <100 mA EnSci; <115 mA SPC)
   - B. Check pump pressure (must be > +50 cm (20 inches) Hg)
   - C. Check pump vacuum. Values depend on site altitude. (Ranges are, for 1000 (780) hPa) < –50 (40) cm (20 (16) inches) Hg)
2. Condition tubing, pump and cathode chamber with very high ozone (> 10 ppmv for 30 minutes)
3. Run on purified air free of ozone for at least 5 minutes
4. Add 3 ml cathode solution (0.5% buffered for EnSci; 1% buffered for SPC)
5. Wait 2 minutes and add 1.5 ml anode solution
6. Run on purified air free of ozone for 10 minutes
7. Run on moderate ozone (5µA) for 10 minutes
8. Run on purified air free of ozone
   - A. Record current after 1 minute running on purified air free of ozone.
   - B. Continue running on purified air free of ozone for 10 minutes and record the background.
9. Add 2 ml more of cathode solution then electrically short cell leads
10. Store in a cool dark place until day of flight.

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[5] *A detailed practical guidance of SOPs for KC96-ozonesonde is given in "Observer's Handbook for Ozonesonde Observation (JMA)" available in Japanese language at the Japan Meteorological Agency, Tokyo, Japan.*

II. Preparation on day of flight:

In the laboratory:

1. Remove both cell caps and place on clean surface
2. Remove and discard the anode and cathode solution
3. Rinse cathode chamber by adding 5 ml fresh cathode solution and remove
4. Add 3 ml fresh cathode solution
5. Add 1.5 ml fresh anode solution
6. Remove electrical short on cell leads and connect leads to test unit
7. Run on purified air free of ozone for 10 minutes
8. Record background current **IB0** (must be <0.05 μA: use digital meter with 0.01 μA resolution)
9. Run on moderate ozone (5 μA) for 5 minutes
10. Record the microamp reading to within 0.01 resolution
11. Switch to run on purified air free of ozone
    A. Record current after 0, 0.5, 1, 3, 5, and 10 minutes on purified air
    B. Current decay should decrease at least 80% in first minute
    C. Record Background Current **IB1** after 10 minutes runned on ozone free air
12. Continue running sonde on purified air. Connect flowmeter to exhaust port of cathode cell. Allow a steady flow of bubbles to thoroughly wet the inside of the burette. Allow about 1 or 2 minutes for the temperature of the glass burette to stabilize
13. Measure 5 flow rates of pump and take average value
14. Record air temperature, pressure and relative humidity in preparation room
15. Calculate the humidity correction based on room temperature and relative humidity of the gas used during flowrate measurement
16. Turn off ozonesonde pump and prepare ozonesonde box for launch.

At the launch site:

17. Turn on radiosonde telemetry system and run on purified air free of ozone for 10 minutes and record background current **IB2**
18. Remove sonde from filtered air and measure surface air until values stabilize , usually 3-5 minutes just prior to launch. However, in cases of strong air pollution or extreme weather situations the launch should be done as fast possible
19. Sonde ready for launch.

III. Post-flight data processing:

1. Use of internal pump temperature $T_{P,Int}$
2. Full background current correction, recommended to use IB2-value (see item 17 in "Preparation on day of flight"). Alternatively, in case IB2 could not be recorded then use a climatological average value of IB2
3. Pump flow efficiency correction pump flow correction at low pressures for SPC-6A *Komhyr* [1986] and ENSCI-Z *Komhyr et al.*[1995] (Table 3.1)
4. Determination of total ozone normalization factor N_{TO} after making all other corrections
5. No use of total ozone normalization factor for linear scaling of vertical ozonesonde profile. Total ozone normalization factor should be exclusively applied as a screening test for overall quality of the profile: $0.9<N_{TO}<1.2$ for ECC-sondes.

A detailed practical guidance of SOPs for ECC-sondes is given in Annex A.

4.6.2 Overview of SOPs for BM sondes

Standard operating procedures for Brewer Mast (BM) ozonesondes briefly described in this Section. A detailed practical guidance is given in Annex B which is an update from an earlier WMO-document (WMO/TD-No.179) by Claude et al. [1986].

Recommendations [*Claude et al., 1986*]:

Essential for proper performance is that brand new- and recovered sondes are prepared equally, i.e. completely disassembled, cleaned, checked and reassembled [See Annex B].

Advance preparation, normally 3-7 days before flight (up to 3 weeks ok):

In the laboratory, after cleansing and re-assembling the device:

(i) Lubricate all pump parts with a whiff of special oil

(ii) Fill the separately stored bubbler with KJ-solution, seal with a teflon cap and store it for a few days in a dark box

(iii) Initial pump test; run on ozonized air with at least 1ppm ozone

(iv) Check polarization voltage of >410mV at the bubbler, exchange KJ-solution

(v) Assemble the bubbler at the pump device

(vi) Run on purified air free of ozone for 5minutes

(vii) Initial system check on the ozone generator with calibrated ozone partial pressure (100nbar) and zero ozone

(viii) Remove the bubbler, seal it with a teflon cap and store it in a dark place until day of flight

(ix) Store pump device in the ozone box, with at least 1 ppm ozone until day of flight.

Preparation on day of flight:

In the laboratory:

1. Final pump test, note down the mean out of 5 measurements, take purified air
2. Check again the polarization voltage >410mV at the bubbler, exchange with fresh KJ-solution (2ml)
3. Assemble the bubbler with the pump device, put both in the corresponding styrofoam box
4. Install the interface and couple the ozonesonde with the radiosonde
5. Turn on radiosonde telemetry system. Check the correct function of interface and radiosonde with a current source connected instead of the bubbler, fixed current: 6microamps
6. Mount the second half of the styrofoam box, make all the devices ready for launch
7. Final check of the entire system at the ozone generator and with purified air free of ozone
8. System ready. Disconnect pump motor wires from the power supply, go to the launch site.

At the launch site:

1. Combine the sondes with parachute and balloon, connect the wires of the pump motor with the power supply. Launch

Post-flight data processing:

1. Pump flow efficiency correction at low pressures for BM-sondes after *Claude et al.,* 1987
2. Determination of total ozone normalization factor N_{TO} first after making all other corrections
3. Use of total ozone normalization factor for linear scaling of vertical ozonesonde profile.

Total ozone normalization factor: $0.9<N_{TO}<1.2$ for BM-sondes. If not, relaunch recommended.

4.6.3 *Overview of SOPs for KC96 sondes*

JMA have participated in JOSIE 1996 [*Smit and Kley*, 1998], JOSIE 2000 [*Smit and Straeter*, 2004] and BESOS 2004 [*Deshler et al.,* 2008]. The results and experiences obtained from these campaigns have been used to better characterize the KC79 sonde, to develop the improved KC 96 sonde and to improve their SOP's for pre-flight preparation and post-flight data processing of the sondes. In this Section a brief summary are given of the revised SOP's for the KC96 sonde as formulated by a group of ozonesonde experts of the Japan Meteorological Agency (JMA).

Recommendations:

1. Composition of the reaction solution

$Na_2HPO_4 \cdot 12H_2O$	17.65 g
KH_2PO_4	7.0 g
KBr	170.0 g
KI	0.2 g
H_2O (liq.)	480.0 cm^3

2. Measurement of cell current I_M and I_{B0} with resolution better than 0.01μA
3. Measurement of reaction solution temperature T_C

Advance preparation

3-8 days before flight

In the observation room:

1. Check pressure sensor of new ozonesonde using a reference pressure gauge (SLP – 5hPa)

2 days before flight:

In the observation room:

1. Degas the carbon electrode in reaction cell
   A. Assemble reaction cell and connect 1 kilo-ohm resistance
   B. Pour reaction solution (until line on the inner wall of cell (approx. 10ml))
   C. Decompress reaction cell (must be < 10hPa (10 minutes))
   D. Check background current (must be between -0.1 and +0.2 μA)
   E. Refill reaction solution (until line on the inner wall of cell)
   F. Store in cool dark place until day of flight

1 days before flight:

In the observation room:

1. Condition tubing and pump
   A. Connect tubing and pump of ozonesonde with ozone generator
   B. Condition tubing and pump with high ozone (approx. 0.8 ppmv for 10 minutes)
   C. Discharge remaining ozone for 10 minutes
2. Confirm the pump flow rate by the digital flow meter calibrated monthly (must be 400 ± 40 cm^3/min)

Preparation on day of flight:

In the observation room:

1. Connect the ozonesonde to the ozone generator
2. Connect the ozonesonde to the ozone calibrator
3. Supply with the electrical power to the ozonesonde
4. Prepare the automatic aerological tracking and receiving system and automatic aerological data processing system for ozonesonde
5. Record ozonesonde signal and check on the pressure and temperature comparing with reference
6. Add a drop of silicon oil to the pump piston and the pump cylinder of ozonesonde
7. Run on purified air free of ozone until the background current is stable
8. Check the background current I_{B0} (must be between -0.1 and +1.0 μA)
9. Record the background current I_{B0} within 0.01 resolution
10. Record the pump flow rate by the digital flow meter
11. Record room temperature and pressure and calculate the pump flow rate
12. Connect the ozone reduction filter to the ozonesonde until the launch
13. Assemble the ozonesonde and prepare for the launch.

At the launch site:

14. Operate the automatic aerological tracking and receiving system and automatic aerological data processing system and start the data sampling of ozonesonde
15. Bring the ozonesonde to the launch site
16. Remove the ozone reduction filter and confirm the increase of reaction current of ozonesonde
17. Launch the ozonesonde
18. Observe the meteorological terms (temperature, humidity, wind components, clouds and weather)
19. Observe the total ozone with Dobson spectrophotometer and record the value of total ozone, observing time and air mass factor
20. Continue the observation until the balloon burst.

Post-flight data processing:

1. Use reaction solution temperature T_C
2. Background current is assumed to be pressure dependent according Eq. 3-10
3. Apply pump flow correction factor C_{PF} (See Eq. 3.10) at low pressures P. Up to 2004 C_{PF} was determined according to Kobayashi and Toyama [1966]:

   $$C_{PF} = 1 - P_{Ref} \times \left(\frac{1}{P} - \frac{1}{P_0} \right)$$

   where P_0 is the pressure at the surface of the launch site and reference pressure P_{Ref} = 2 hPa. Based on new insights made during JOSIE and BESOS an experimentally determined pump efficiency C_{PF} is applied as part of a new data reduction algorithm (AKC-2004 algorithm), which is briefly described below and in more detail by Fujimoto et al. [2004]
4. Determine total ozone normalization factor N_{TO} first after making all other corrections
5. Use total ozone normalization factor for linear scaling of vertical ozonesonde profile
6. A detailed practical guidance of SOPs for KC96-ozonesonde is given in “Observer’s Handbook for Ozonesonde Observation (JMA)” available in Japanese language at the Japan Meteorological Agency, Tokyo, Japan.

4.7 Near Real Time Use of Ozone Sounding Data

Near real time (NRT) access to ozonesonde data is getting more and more of crucial importance with regard to new and future applications. The GAW/IGACO goal for improving predictive capability and increased use of assimilation schemes will increase the need of NRT data in the future. A first step had been made at the joint ECMWF/WMO expert meeting on real time exchange of ground based ozone measurements, held at ECMWF in 1996, the requirements for ozone data for numerical weather prediction (NWP) in real time were outlined. ECMWF has developed the operational data assimilation system to include ozone retrieval from satellite such as SBUV and GOME, and requires independent high quality profile data from ground-based systems [e.g. *Dethof and Holm*, 2004]. For daily validation, monitoring and trouble shooting, ozonesonde data have to be available at the ECMWF within 12–24 hours after the sounding. Nowadays, weather forecasting centres also including air quality in their operational forecasting products such that there is a growing interest in assimilating NRT-ozonesonde profiles [e.g. *Fleming et al.*, 2011]. At present the Norwegian Institute of Air Research (NILU) runs a service to collect the sonde data from different sounding stations and provide the data in a proper data format to ECMWF. A number of registered stations (mostly in Europe, but also some others) submit an ozone sounding data file to NILU within a few hours after a completed sounding. The file format used is NASA Ames 2160. Every 15 minutes, a programme automatically scans through the various directories and locates new files. These files are then read and checked for errors and the data file is converted to the CREX format. CREX files are put on a separate directory where ECMWF picks them up every 30 minutes. The programme performs some simple checks on the data (e.g. to ensure the electrolyte was not frozen during the flight) and the total ozone column is calculated if the balloon reached sufficient altitudes. The programme currently only outputs files in CREX format, which is then converted to BUFR by ECMWF, but the programme may also output the files as HDF/netCDF files. The input data format is NASA Ames 2160, but NILU has also developed an alternative version of the software that accepts the format used by WOUDC.

Although, many European and North American sounding stations provide already fast NRT data but more stations should be capable of providing data in near real time [*IGACO-O3 and UV Implementation Plan*, 2007].

4.8 Data archival: Specifications for Submission to WOUDC

4.8.1 Introduction

Access to high resolution vertical profiles of ozone measured with sondes is a key point for all users from research scientists to policy makers. Ozonesonde data are archived at the World Ozone and UV Data Centre (WOUDC), which is operated by the Experimental Studies Section of Environment Canada and is located in Toronto. The WOUDC began as the World Ozone Data Centre (WODC) in 1961 and produced its first data publication of Ozone Data for the World in 1964. In June 1992 ultraviolet radiation data was added to the data centre and has since been renamed to the World Ozone and Ultraviolet Radiation Data Centre (WOUDC) with the two component parts: the WODC and the World Ultraviolet Radiation Data Centre (WUDC). The ozone data archive contains following data categories: Lidar vertical profiles, Ozonesonde vertical profiles, Total column ozone (Daily and Monthly values) and Umkehr N-value and C-Umkehr vertical profiles. The UV data archive contains Broad band, Multi band and Spectral data.

Since methods and capacity to archive data has been improved drastically since 1990's this enables to store full resolution sounding data together with detailed supporting documentation about data origin, content and quality which will improve the long term traceability significantly. The ASOPOS panel recommended to apply a new ozonesonde data format for archiving that particularly emphasizes on the traceability of the archived ozonesonde data through: (i) extending the suite of parameters obtained from pre-flight preparation as well as including in the (vertical) profile data in-situ measured parameter like ozonesonde cell current or pump motor current; (ii) meta data documenting the state of the art of the station (logbook of instrumental, preparational and correctional procedures). This would allow that at any later time the archived vertical ozone profile data can be re-processed from its original measured parameter such as the non-corrected, i.e. raw, ozonesonde cell current and its supporting temperature and flowrate of the air sampling pump, but now applying different correctional procedures according new in-sights on the performance of the sonde.

Consequently, this has required a complete revision of the ozonesonde data format for submission to the WOUDC. The primary purpose of the new format is to provide level 1.0 quality controlled vertical profile data to end users that are interested in ozone for scientific research. Secondary, but important purpose is to provide also engineering data to end users to assess the performance of ozonesondes and their archived profile data in more detail. This also provide the opportunity to re-process the sonde profile data according new insights on the performance of the sonde and the methodology of post-flight data processing. A file format designed for both will have to be a compromise between the need for a simple summary of the data and the need for as much secondary information as possible. During the processing of an ozonesonde flight, decisions are made over what data is valid, questionable, completely erroneous, incomplete, interpolated, recorded before release, or some combination of these. For the first type of user these issues are of no direct interest, but they are of vital importance to the second type of data user assessing the performance of the ozonesoundings and their archived data.

One way of indicating which data is in which category is to use flags. The problem with flags is that it requires that the end user actively filter the data – a potential trap for the unwary. Also, if different users pick different flags the results of their analysis will be different based on the same data. Fortunately, in practice the only criterion that most users will be interested in is whether the data is valid or not. This binary condition suggests an alternate way of organizing the file; put validated vertical sounding (= ***#Profile***) data in one table (as in the previous WOUDC format) and put the rest of the recorded sounding data in a similarly formatted but separate table for the users that need the complete record. This hides much of the complexity of the data from the majority of users while providing only a very modest obstacle to users interested in a more detailed analysis or re-analysis. This means that next to the ***#Profile***-data (validated and provided by the sounding station) now two new ***#PreLaunch***- and ***#DeSelected***-data blocks have been added.

The ***#PreLaunch*** data block (if available) contains the measured parameters (listed in #PROFILE segment) as recorded about 20 minutes before until launch. In the future these data will play an important role when using deconvoluting data processing techniques to resolve ozone sonde memory effects (See Sections 3.2.3 and 3.2.6).

The ***#De-Selected*** data block contains information of interest to specialized users, a more comprehensive set of data flags would be included. These could include flags for instrument temperature too high or too low, data invalidated by automatic QC routine, data invalidated by data originator, and other options that are related to operational issues so that the file can be used for QA purposes. The flag used in the validated profile data – ***"LevelCode"*** currently just indicates if a level in the profile is an inflection point or a WMO standard level. However, in the new format this parameter will be also used as that additional flag to characterize the individual measured data points more specifically

Also new is the ***#Profile_Uncertainty*** data block that will contains the estimated uncertainty (if available) for each of the measured profile parameters as a function of ***Duration*** as listed in ***#PROFILE*** segment. The general guidelines to determine these uncertainties are in preparation and will become soon avalaible as a separate GAW-report.

In collaboration with NDACC (former NDSC)- and SHADOZ- ozonesonde networks the following decisions and recommendations of data archival - requirement - to include all information needed to process/reprocess the data were made. An ozonesonde data file should contain the following four main data segments: (i) Overhead (ii) Header, (iii) Profile, and (iv) Meta, which are briefly documented in this Section.

4.8.2 Overview of major specifications on new ozonesonde data format

I) Overhead Segment: Administrative & instrumental information

#CONTENT

- Specifications on type of WOUDC-data: ***Class, Category, Level, Form***

#DATA_GENERATION

- Specifications of data provider: ***Date, Agency, VersionNumber, ScientificAuthority***

#PLATFORM

- Specifications on type of measuring platform: ***Type, ID, Name, Country, GAW_ID***

#INSTRUMENT

- Specifications on ozonesonde: ***Name, Model, Number***

#LOCATION

- Geographical location of launch platform: ***Latititude, Longitude. Height***

#TIME_STAMP -

- Specifications of launch time: ***UTCOffset, Date, Time***

II) Header Segment: Data of pre-flight preparation and post-flight data processing

#PREFLIGHT_SUMMARY

- ***Ib0*** [micro-amps=10^{-6} A] - Background current of ozonesonde measured in the laboratory before sonde is exposed is to ozone
- ***Ib1*** [micro-amps=10^{-6} A] - Background current of ozonesonde measured in the laboratory after sonde is exposed is exposed to defined dose of ozone
- ***Ib2*** [micro-amps=10^{-6} A] - Background current of ozonesonde measured at the field site just prior to launch
- ***SolutionType*** - Chemical composition of sensing solution of ozonesonde
- ***SolutionVolume*** [ml] - Volume amount of sensing solution of ozonesonde
- ***PumpFlowRate*** [cm3/min] - Pump flowrate measured in the laboratory at surface conditions (corrected for moistening: see Section 3.2.4)
- **OzonesondeResponseTime** [min] - Response time (1/e) measured in the laboratory from decay test at initial 5µA cell current using purified ozone free air

#RADIOSONDE -

- Specifications on radiosonde: ***Name, Model, Number***

#INTERFACE_CARD

- Specifications on interface card: ***Name, Model, Number***

#SAMPLING_METHOD

- ***TypeOzoneFreeAir*** - Techniques to obtain ozone free air at the launch site just prior to launch
- ***CorrectionWettingFlow*** - Correction used for wetting flow when using non-saturated air during pumpflow measurement as part of pre-flight preparations
- ***SurfaceOzone*** [ppbv] - Surface ozone volume mixing ratio measured by independent method
- ***DurationSurfaceOzone*** [min] - Time taken to stabilise ozonesonde prior to launch.

- ***MinutesGroundO3*** [min] - Time that ozonesonde is exposed to surface ozone
- ***LengthBG*** [m] - Distance (length) between the bottom of the balloon and the sonde payload (gondola)
- ***WMOTropopausePressure*** [hPa] - Ambient air pressure at the tropopause which is determined after WMO-definition.
- ***BurstOzonePressure*** [mPa] - Ozone partial pressure at balloon burst altitude
- ***GroundEquipment*** - Basic ground equipment
- ***ProcessingSoftware*** - Post flight processing software

#Pump_Settings

- ***MotorCurrent*** [mA] - Electrical current through pump motor
- ***HeadPressure*** [hPa] - Maximum pressure when outlet of pump is stopped
- ***VacuumPressure*** [hPa] - Minimum pressure when inlet of pump is stopped

#Pump_Correction

- Correction table ***{Pressure[i], PumpCorrectionFactor[i]}*** for degradation of pump flow efficiency at lower pressures

#FLIGHT_SUMMARY

- ***IntegratedO3*** [DU] - Vertical ozone column integrated from launch platform to balloon burst altitude
- ***CorrectionCode*** - Code for the method applied to estimate the remaining ozone (calculated residual) above balloon burst altitude to the top of the atmosphere
- ***SondeTotalO3*** [DU] - Total vertical ozone column: Sum of integrated profile and calculated residual.
- ***NormalizationFactor*** - Ratio of total ozone column measured by spectrophotometer (e.g. Dobson or Brewer) and total ozone column derived from ozonesonde profile.
- ***BackgroundCorrection*** - Background current correction method applied
- ***SampleTemperatureType*** - Thermistor position (box, pump, inlet tube, estimated or constant) to measure the temperature of the sampling air through the pump

#Ozone_Reference

- Total ozone column as measured by independent instrument (e.g. Dobson or Brewer) plus specifications on instrument and measurement made.

III) Profile Segment: Vertical profile data (including uncertainties)

#PROFILE

1. ***Duration*** [second], i.e. elapsed flight time as primary variable [second]
2. ***Pressure*** [hPa]
3. ***O3PartialPressure*** [mPa], i.e. ozone partial pressure after all corrections applied
4. ***Temperature*** [K]
5. ***WindSpeed*** [m/s] , i.e. wind speed (if available)
6. ***WindDirection*** [degrees in 360], i.e. wind direction (if available)

7. ***LevelCode*** , i.e. in the elder soundings before 1990's this coded identifier is used to characterize parts of the profile, while in modern soundings here it can be also applied to characterize each individual ozone measurement of the vertical profile.
8. ***GPHeight*** [m], i.e. geopotential height
9. ***RelativeHumidity*** [%], i.e relative humidity in percent with respect to liquid water
10. ***SampleTemperature*** [K], i.e. temperature of air sampled by pump, usually the pump temperature
11. ***SondeCurrent*** [micro-amps= 10^{-6} A], measured ozonesonde current (**no** corrections applied)
12. ***PumpMotorCurrent*** [mA] (if available), i.e. electrical current measured through the pump motor
13. ***PumpMotorVoltage*** [V] (if available), i.e. applied voltage measured across the pump motor
14. ***Latitude*** [-90 to +90 degrees] (if available), i.e. geographical latitude (e.g. GPS)
15. ***Longitude*** [-180 to + 180]) (if available), i.e. geographical longitude (e.g. GPS)
16. ***Height*** [masl = meter above sea level) (if available), i.e. geographical height (e.g. GPS)

#PROFILE_UNCERTAINTY

- Estimated uncertainty (if available) for each of the measured profile parameters as listed in ***#PROFILE*** segment.

 # PreLaunch

- Pre-launch data (if available) for each of the measured parameter (listed in ***#PROFILE*** segment) as recorded 15-20 minutes before launch. At launch the Duration is zero, while before launch the ***Duration*** is relative to launch and thus negative in sign.

 # DeSelected

- Deselected data records (if available) of the measured profile parameters (listed in #***PROFILE*** segment) that have been de-selected from the original profile data after validation or filtering of the data on their correctness. Hereby the profile parameter ***LevelCode*** will be used as an index table indicating the reason for de-selection of the data record

IV) <u>Meta Data Segment:</u> Information characteristic of the station

A new and important aspect is that there should be a link from individual sounding data set to a meta file having following structure:

a) **General information**: description of station and the specifications of the sounding system used, operating procedure followed at present state, but in a historical perspective. Here the sounding station can also add new information on fundamental changes done. Free ascii text format

b) **Logbook**: reporting specific information on changes of sounding system , preparing sonde procedures, or data processing procedures. Free ascii text format.

5. DATA QUALITY INDICATORS (DQI)

5.1 Introduction

There are several ozone data product categories defined by the WOUDC: total column ozone and vertical profile information from ozonesondes and Umkehr/Lidar retrievals mostly from ground-based, stationary platforms. Ozonesondes have their own unique data content with its own specific indicators. The new and more advanced structure of the revised ozonesonde data format at WOUDC with the four major data segments: (i) Overhead (ii) Header, (iii) Profile, and (iv) Meta (Section 4.8) includes additional information to be used to process, reprocess and evaluate the data on their reliability. The purpose of this chapter is to give some guidelines to the user of ozonesonde data in the form of data quality indicators (DQI). The intention is to use the DQI as a means to make an objective assessment of the quality of the individual sonde data archived in the WOUDC that is based on what is known about the data sets. This might be done at three levels: (i) DQI's for "screening" individual vertical profiles of the sonde performance and the precision and accuracy to be expected (ii) Tools to homogenize long term records of a single sounding stations or to homogenize data records of different sounding stations (iii) DQI's for "screening" on more general aspects such as station information and its sounding practice, traceability, data re-processing and data usage.

5.2 Screening individual vertical ozonesonde profiles

Each ozone sounding is made with a new instrument, which therefore has to be characterized properly prior to flight. Post-flight characterization, however, is not possible such that only pre-flight and in-flight sounding data can be used to screen the individual sounding data on their reliability. Table 5-1 contains quantitative criteria to screen the quality of an individual vertical ozonesonde data profile. These criteria are not a guarantee but serve as more or less objective indicators on the performance of the sonde and the reliability of the individual sounding data.

Table 5-1: Screening criteria to test the reliability of individual vertical ozonesonde data profiles made with major ozonesonde types used in GAW-ozonesonde network (For details see text Section 5.2)

Indicator	ECC SPC	ECC ENSCIZ	BM	KC79/96	*Identifier in WOUDC*
Total ozone normalization factor	0.9-1.1	0.9-1.1	0.8-1.2	0.8-1.2	*TotalOzoneNormalizationFactor*
Pump flowrate [ml/min]	210 - 230	200-220	200-230	100-120	*PumpFlowRate*
Response time (1/e)[s]	20-30	20-30	20-30	40-50	
Pump temperature [K]	273-310	273-310	273-310	273-310	*SampleTemperature*
Pump temperature measurement method: In-flight (location), Table, Constant					*SampleTemperatureType*
Background current IB1 [µA]	0-0.10	0-0.105			*Ib1*
Background current IB1ae [µA]	0-0.15	0-0.015			*Ib1ae*
Background current IB2 [µA]	0-0.15	0-0.15			*Ib2*
Sensing solution type (SST)					*SensingSolutionType*
Pump motor current [mA]	>100 mA	>90 mA			*PumpMotorCurrent*

Total ozone normalization factor *(See also Section 3.2.7)*

The total ozone normalization factor (N_T) is by definition the ratio of total ozone column measured by spectrophotometer (e.g. Dobson or Brewer) and total ozone column derived from ozonesonde profile plus estimated residual above balloon burst height. The factor provides a good screening test for unreliable soundings using the criterion that the normalization factor may not deviate more than about ±(0.1-0.2) from one [*Tiao et al.,* 1986]. However, a normalization factor of one is not a guarantee that the profile is correct. In routine operation the normalization factors for ECC-sondes are in the range of 0.9-1.1 while BM-and KC-sondes show normalization factors of 0.8-1.2 [*SPARC-IOC-GAW*, 1998].

Optionally ozonesonde profiles are normalized, whereby the ozonesonde profile is linearly scaled by the total ozone normalization factor (N_T). The use of the normalization to adjust the profile is controversial due to the fact that the electrochemical ozonesonde is in principle an absolute measuring device. If the total ozone normalization factor (N_T) is negative, it means that the factor has not been applied to linear scale the vertical ozonesonde profile.

Pump flowrate *(See also Section 3.2.4)*

Volumetric flowrate of air sampling pump is measured at surface (i.e. laboratory) conditions as part of the pre-flight preparation of each individual flown ozonesonde. At ambient air pressures below 100 hPa the efficiency of the gas sampling pump decreates for which is corrected for by applying a pump correction factor C_{PF}, which is as function of ambient pressure specific for each sonde type. The correction tables (See Table 3.2) are based on empirical averages obtained from pump flow efficiency measurements made at different air pressures in the laboratory [*SPARC-IOC-GAW*, 1998]. The uncertainty of the correction factors presented increases substantially at pressures below about 20 hPa which can contribute significantly to the overall uncertainty of the sonde performance above 25-30 km altitude. The uncertainty of the pumpflow efficiency is one of the most prominent contributions to the overall uncertainty of the sonde measurements above 25 km altitude.

Response time *(See also Section 3.2.6)*

The in-flight response time to a step change is approximately 20-30 s (<1 min) for the ECC- and BM-sonde types, and 40-50 s (<1 min) for KC79/96 sonde. At a typical ascent velocity of 5m/s this translates into an altitude resolution of about 100 m for ECC and BM and 200 m for KC96 and a slight displacement of the profile in the vertical relative to the actual profile. The usual practice is to make no correction for the lag in response. Usually, response times larger than 1 min is a strong indication of malfunction of the ozonesonde producing non-reliable data.

Pump temperature *(See also Section 3.2.5)*

To correct for changes of the air mass flow rate through the sensor due to temperature changes the actual pump temperature is measured in-flight either inside the pump or in the instrument enclosure (Styrofoam box). Over the course of a sounding the pump temperature can change typically by 10-25°C. In older sounding systems used before the 1990's it was not possible to measure the actual pump temperature due to the limited number of signals the analog operating radiosondes were capable of transmitting. Therefore, it was common practice that either a constant pump temperature or an empirical table of the pump temperature as a function of ambient air pressure was applied. This can introduce uncertainties of 1-7% in the ozone computations, particularly for the highest altitudes [*SPARC-OTA-GAW*, 1998]. The in-situ pump temperature should never be below 273 K the freezing point of the sensing solution (≈273 K) because this will cause freezing of the sensing solution, i.e. malfunction of the ozone sensor cell and thus produce erratic ozonesonde data. On the other hand the higher the pump temperature the faster the sensing solution will evaporate over the course of the sounding that may introduce large uncertainties in the conversion efficiency of the ozone sensor (See Section 3.2.2).

Location of pump temperature sensor *(See also Section 3.2.5)*

In modern soundings the temperature itself can be measured with an accuracy better than 1-2 K, however, the location of the pump temperature sensor can be still an additional source of uncertainty. To measure the temperature inside or outside the pump can differ significantly from values of ≈1K near the surface and increasing up to values of ≈5-10K at lower pressures (See Figure 3-3). A common procedure for measuring the pump temperature was to tape a thermistor to the outside of the Teflon block of the pump near to and at the same height as the tube outlet from the block (going to the cathode cell) - henceforth known as the 'external pump temperature'. Nowadays, both ECC-sonde manufacturers provide their sondes with a hole drilled into the Teflon block. This allows the thermistor to be positioned close to the piston and to measure the appropriate 'internal pump temperature'.

Pump motor current

Usually a 12 VDC electric motor drives the air sampling pump of the ozonesonde. The electrical current should range within the values as given in Table 5.1. Large currents may indicate excessive frictional heating of moving parts of the pump causing a loss of pump efficiency while too low motor currents can be symptomatic for any pump leakage, i.e also loss of pump efficiency. In both cases the ozonesonde data will tend to be too low. In conjunction this may be indicated by a total ozone normalization factor larger than 1.0.

Background current *(See also Section 3.2.3)*

As part of the pre-flight preparation of the sonde the background current of each ozonesonde is individually recorded by forcing ozone free air through sensor cell. Excepted are the Brewer-Mast sondes where prior to flight the sonde readings are electronically compensated for the background current. For ECC-ozonesonde types the background signal is correlated with past exposure to ozone. AS a consequence up to three different background currents may have been measured and archived, namely in the laboratory before and after exposure of zone (ib1 and ib1ae respectively.) and optionally at the launch platform just prior to flight (ib2). Although the background currents of the SPC-6A and ENSCI-Z sondes are of the same magnitude, they both are significantly larger after exposure to ozone (Table 3-1 in Section 3.2.3, *Smit et al.*, 2007) This enhancement effect of the background current, from values 0-0.05 μA (≈0-0.2 mPa ozone partial pressure equivalent) before ozone exposure to 0.05-0.11 μA (≈0.2-0.4 mPa ozone partial pressure equivalent) after exposure to ozone, is poorly understood [*SPARC-OTA-GAW, 1998*]. In elder ECC-soundings, before about 1990, the background currents were generally about factor 2 larger than after that date. There is no clear explanation for this effect .However, background signals should not exceed 0.2 μA otherwise this may be an indication of malfunctioning of the sonde producing non-reliable profile data.

Sensing solution type (SST) and ECC-sonde type *(See Section 3.2.2)*

This concerns exclusively the ECC-ozonesonde types. Before 1995 only one manufacturer existed producing the SPC-sonde type (See Table 2-1, Section 2.3.1) Since 1995 two different manufacturers of ECC-ozonesondes producing the SPC-6A and ENSCI-Z sonde types, respectively. JOSIE 2000 and BESOS experiments [*Smit et al.*, 2007; *Deshler et al.*, 2008] demonstrated that significant differences in the ozone readings occur when ECC-sondes of the same type are operated with different cathode sensing solution strength (Table 2-2, Section 2.3.1). For each ECC-manufacturer type the use of 1.0% KI and full buffer (SST1.0) gives ≈ 5% larger ozone values compared with the use of 0.5% KI and half buffer (SST0.5), and as much as 10% larger values compared with 2.0% KI and no buffer (SST2.0) [Smit et al., 2007]. JOSIE demonstrated that the performance characteristics of the two ECC-sonde types can be significantly different, even when operated under the same conditions. Particularly above 20 km the ENSCI-Z sonde tends to "measure" 5-10 % more ozone than the SPC-6A sonde. Below 20 km the differences are 5 % or less, but appear to show some differences with year of manufacture. Before 1995 the SPC-(3A,4A,5A) sonde types were mostly flown with1.0% KI and full buffer (SST1.0). However, in the 1970's and early 1980's ECC-sondes were operated with higher concentrated sensing solutions with strengths of factor 1.5 or even 2.0 higher than compared to SST1.0.

5.3 Homogenization of temporal and spatial ozonesonde records

JOSIE [*Smit et al.,* 2007] clearly demonstrated that with regard to the sonde performance and hence the interpretation of ozone trends caution has to be exercised in making instrumental changes or in preparing/operating procedures. However, during the last decade several changes of operating procedures for ozonesondes were introduced such that at present, a variety of preparatory and corrective methods are applied by the different sounding stations. This can cause artifacts in the time series of a single station but station to station ozone variability, which may have a dramatic impact on the derivation of long term ozone trends. Therefore quantitative tools are needed to homogenize: (i) long term records of individual sounding stations; (ii) sounding records between different station. Important tool thereby are "transfer functions" which describe the quantative differences of the sonde response based on changes of the instrument or operating procedures.

Examples of individual sounding stations like Uccle (Belgium) or Payerne (Switzerland) which homogenized their long term ozone records are given in literature by *DeBacker et al.* [1998, 1999] and *Jeannet et al.* [2007], with special emphasis on their changing from Brewer-Mast to ECC sondes (See also Section 4.3). At present as part of the SPARC/IGACO-O3/IOC initiative on

"Understanding past changes in the vertical distribution of ozone" a working group is deriving and evaluating empirical transfer functions for different types of ozonesondes in order to homogenize long term ozone soundings records in both temporal as well as spatial perspective. Hereby the work is focused on the ECC-sonde type with different manufacturers and different sensing solution types

5.4 General DQI's for Ozonesondes

General DQI are categorized in: (i) Station information and its sounding practice; (ii) Traceability; (iii) Data re-processing; (iv) Data usage. General DQI are not quantitative but only qualitative indicators which still can give valuable information about the profiling capabilities of an individual sounding station and its sonde data quality, this also in long term perspective. However, these are only indirect indicators and need to be applied very carefully in order to avoid any form of subjectivity. In the next Sections the four major categories of general DQI's are described in more detail.

5.4.1 Station information and its sounding practice

This is typically a 2-3 page text document made available at the WOUDC describing the station, its sounding system and its practice of preparation, operation and post-flight processing. Platform considerations about its geographical location, air quality (industrial or natural pollution).

5.4.2 Traceability

Particularly for long term sounding records traceability is crucial. Intercomparison campaigns like JOSIE and BESOS have shown that small changes in instruments or operating procedures can have significant impact on long time record of a sounding station and the long term trend derived from these records. Important aspects of traceability to consider are:

(i) Long term record of changes in sounding system, methodology followed of preparation, operation and post-flight processing
(ii) Comparison with other profiling techniques like ground based Lidar or Micro-wave techniques or satellites

5.4.3 Data reprocessing

Documentation of data processing and particularly revisions, important thereby is that there is an unique version number of the data sets linked to the documentation of data processing cq. data revision. This is also important in historical perspective with regard to the evolution in data processing and eventual influence on long term trends derived from the time series of ozone soundings of the station.

5.4.4 Data usage

Data usage can be referring to the use of station sounding data for:

(i) Scientific publications (especially in refereed journals)
(ii) Instrumental publications assessing the performance of the sonde used at the station

These publications might refer to problems within data sets or conversely demonstrate the high quality of a particular record. It is important to know that a data record has already been analysed by someone in an independent study, especially an expert, so that the same problems do not have to be "rediscovered". Inclusion of these data sets within the WOUDC is also recommended.

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Standard Operating Procedures For ECC Ozonesondes

A practical guidance

Lead authors

Bryan Johnson (NOAA/GMD, Boulder, USA)
and
Jonathan Davies (EC, Toronto, Canada)

Table of Contents

A-1 Basic ECC ozonesonde principles

The ozonesonde conditioning and preparation procedures outlined in this Standard Operating Procedure (SOP) are designed to obtain accurate and reproducible ozonesonde measurements and to reduce the uncertainties by following a consistent procedure for each ozonesonde being prepared. The ozonesonde measurement, described below, depends on proper sensor output and accurate flow rates. Eliminating or preventing contamination of the ozonesonde Teflon parts and sensor is an important first step in the SOP. Therefore, high ozone conditioning, use of clean zero-ozone air, and use of pure distilled, de-ionized water for KI sensor solutions all help to reduce uncertainties in the sensor operation so the current is more representative of the true ambient ozone levels. It is also important to recognize potential pump problems by checking the pump current, pump pressure, and vacuum. And finally, background currents are reduced by charging the sensor with cathode and anode solutions several days in advance of the actual balloon flight and changing solutions on the day of flight. This extra time allows the sensor cell to equilibrate and the ion bridge to fully saturate. Shorting the cell leads during instrument storage also aids in reducing the background.

The electrochemical concentration cell (ECC) ozonesonde instrument consists of a Teflon piston pump which continuously bubbles ambient air into an ozone sensor. The sensor consists of cathode and anode chambers containing platinum electrodes immersed in solutions of potassium iodide (KI). The chambers are linked by an ion bridge to allow for the flow of ions. Ozone immediately reacts with iodide in the cathode solution by the reaction:

$$2KI + O_3 + H_2O \rightarrow I_2 + O_2 + 2KOH$$

The production of I_2 during the above reaction generates a slight shift in the equilibrium between the cathode (dilute KI) and anode (saturated KI) chambers. The cell then responds by converting the iodine back to iodide producing a microamp current, which is directly proportional to the ozone mass flow rate bubbled into the cathode solution.

The cell microamp current is converted to ozone partial pressure from Equation (1). The calculation also requires the background current (sampling ozone-free air) and the ozonesonde pump volume flow rate which are measured during the final pre-flight preparation. During the actual balloon ascent, the pump temperature (measured by a thermistor in the Teflon pump block) will decrease or increase so a correction for gas density enters into equation Eq. A-1 by multiplying by the pump temperature in degrees Kelvin, with the assumption that the pump temperature is nearly equal to the temperature of the gas that is inside the pump piston volume.

A second correction factor in Eq. A-1 is the correction for the decrease in pump efficiency at low pressures (less than 300 hPa) (Eq. A-2].

[Eq.A-1] $$\mathrm{P_{O3}} = 0.043085 \cdot \frac{\mathrm{T_P}}{(\eta_\mathrm{C} \cdot \Phi_\mathrm{P})} \cdot (\mathrm{I_M} - \mathrm{I_B})$$

Where:

P_{O3}	Ozone partial pressure (millipascals)
I_M	Cell output current (microamperes)
I_B	Cell background current (typically 0-0.1 microamperes)
T_p	Temperature of sonde pump (K)
η_C	Conversion efficiency: usually equal to 1.00
Φ_P	Pump volume flow rate (cm^3/s)

[Eq.A-2] $$\Phi_\mathrm{P} = C_{PF} \bullet \Phi_\mathrm{P,\ Ground}$$

whereby C_{PF} is the correction factor for declining pumpflow efficiency at lower pressures. Recommended is to use the pumpflow efficiency correction pump flow correction at low pressures for SPC-6A Komhyr [1986] and ENSCI-Z Komhyr et al.[1995] (Table 3.1).

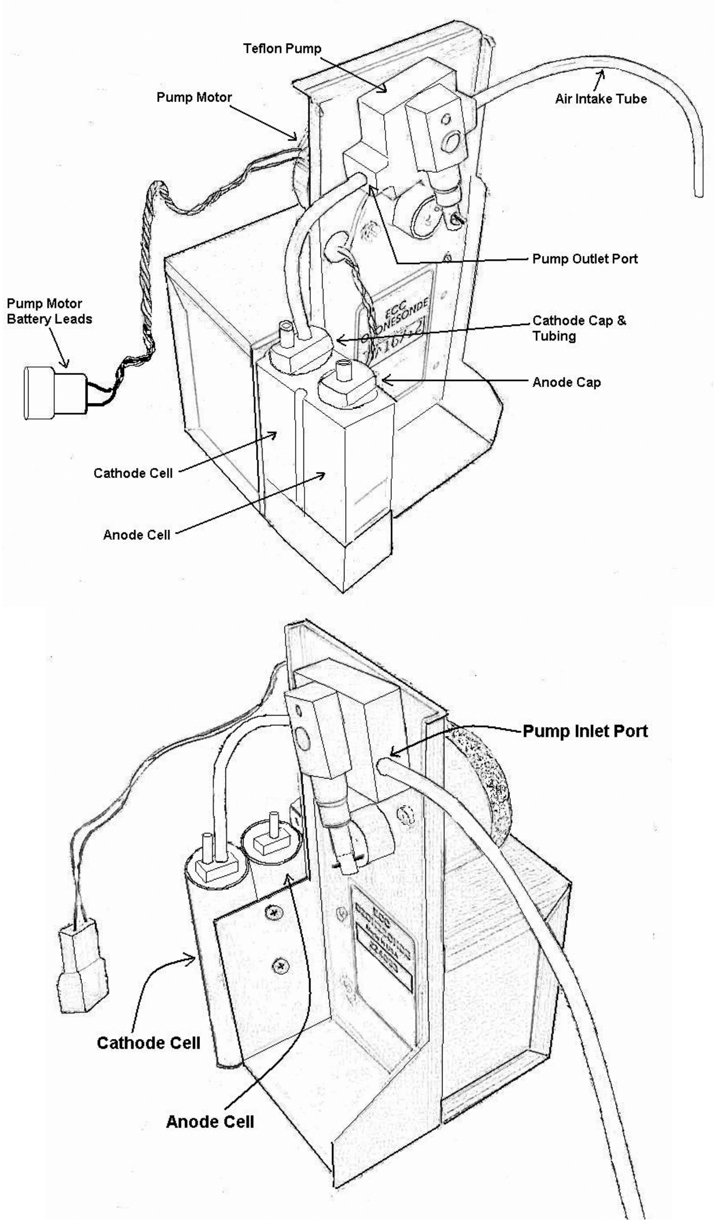

Figure A-1: Two ECC ozonesonde instruments. Note that the cathode cell may be either on the left or right side, depending on the manufacturer

A-2 Advanced Ozonesonde Preparation *(3-7 days before flight)*

The advanced preparation steps are the first check on the ozonesonde pump and sensor cell performance. The addition of the sensor solutions several days before the actual balloon flight allows the cell to attain a low background current. Preparation should be done in a clean room environment.

A record of the pre-flight preparation should be made using a checkout sheet and this should be kept in an archive for future reference.

An example checkout sheet is included as part of this report.

In the example sheet each empty box should be filled in with a value from the pre-flight test and the empty circles are checked off when the indicated step is completed. There is also a panel on the sheet for recording factory information for the ECC sonde and Vaisala interface (if used) which can be written down.

An electronic count-down timer is a useful aid for some of the following steps.

1. Begin a new ozonesonde check list.

2. Switch ‘ON’ the ozonizer/test unit power and air pump to begin zero ozone air flow.

3. Remove the ozonesonde from the white polystyrene box. Connect the ozonesonde intake tube to the pump intake port side of the ozonesonde Teflon pump. Disconnect the cathode tubing from the pump outlet port

4. Connect the ozonesonde pump motor leads to ozonizer/test unit 12 volt DC power terminals. Insert the intake tube into the no/low ozone outlet. Switch on ozonesonde power and run for 10 minutes sampling clean, zero ozone air. At the end of this period record the initial motor current (proper current should be < 100 mA). Then disconnect the intake tube, and with a pressure/vacuum gauge measure:

   a) Pump Head Pressure from pump outlet (“over” pressure should be > 700 hPa excess to laboratory pressure)
   b) Pump Vacuum from pump inlet port (“under” pressure should be more than 500 hPa lower than laboratory pressure)

5. Re-connect the ozonesonde air intake tube and the cathode tubing. Insert the intake tube into the high ozone outlet of the ozonizer/test unit. Turn on the UV lamp and fully pull out the ozone control/shield tube. Turn on the ozonesonde pump and sample high ozone for 30 minutes to condition the intake tube, pump, cathode tubing and cathode cell chamber. Switch off the ozonizer/test unit air pump during this period. Avoid breathing the high ozone air exhaust or connect the cathode exhaust tubing to a Drierite desiccant column or other filter.

6. Turn the ozonizer/test unit air pump back on. Turn off the UV lamp and push the ozone control shield all the way back in. Withdraw the intake tube from the high ozone outlet and move into the no/low ozone outlet. Run for 5 minutes sampling clean, zero ozone air.

7. Remove the cathode and anode caps and place them on a clean surface, taking care not to handle the lower parts that normally sit inside the cell. Add 3 ml of cathode solution to the cathode cell using a syringe reserved for this purpose. Replace the cathode cap by carefully sliding the long section of the tube over the Teflon rod protruding up from the bottom of the cell. Only when the tube is positioned correctly by the rod can the cap be pushed safely all the way into the top of the cell. Wait 2 minutes to allow the cathode solution to permeate the ion bridge. Then add 1.5 ml of anode solution to the anode cell using a separate syringe reserved for anode solution then replace the anode cap.

8. Disconnect the cell sensor leads from the electronic interface board and connect to the ozonizer/test unit microammeter leads. Run the ozonesonde for 10 minutes while sampling clean, zero ozone air.

9. While the ozonesonde continues to sample air from the no/low ozone port, turn on the UV lamp on the ozonizer test unit and pull out the ozone control shield about 3 to 4 cm. Make additional adjustments to the position of the ozone control shield until a relatively steady current of 5 µA is observed on the microammeter. Continue sampling for 5 minutes making small adjustments to the ozone control shield as necessary.

10. After 5 minutes have elapsed then SIMULTANIOUSLY turn off the UV lamp and start the stopwatch. Check that the microamp current drops by 70-80% in one minute (5 µA to 1.0 - 1.5 µA). Continue sampling clean, zero ozone air for 9-10 minutes. The microammeter reading will slowly decay to values within the 0.2 to 0.6 µA range.

11. Turn off all ozonizer/test unit switches.

12. Nearly fill the cathode cell by adding about 2.5 additional ml of cathode solution. Connect a shorting plug to the ozonesonde cell leads. Store the ozonesonde inside a plastic bag in a dark, clean environment.

***Note**: Rinse syringes with distilled water after use. Place the bottle caps back on cathode and anode solution bottles immediately after use.*

A-3 Final Pre-Flight Preparation *(Preparation Day of Flight)*

These final pre-flight procedures are to be completed less than 24 hours before the sonde is launched but in case of a delay can be repeated.

On the day before release you should have on hand two or more instruments which have been checked for proper operation (from advanced ozonesonde preparation) and filled with sensing solution at least three days earlier. Use the sonde that has been filled with solution for the longest time first. Stored instruments should have solutions replaced approximately every two weeks.

A-3.1 Change the sensing solutions

13. First, remove the sonde from the plastic bag and Styrofoam flight box and disconnect the shorting plug Inspect the cell caps for KI salt crystals or white film. If either of these is present rinse them away with distilled water and wipe dry the anode and cathode caps with a clean, lint free tissue before removing them.

14. Disconnect the cathode tubing from the outlet (exhaust) port of the Teflon pump then using a pair of small pliers, remove the cathode cap from the cell. While holding the cap with the pliers rinse the section of tubing that normally sits inside the cathode chamber solution and shake off the excess droplets from the rinse solution.

15. Place the cathode cap on a clean surface, again taking care not to handle the lower parts. Remove the anode cap and place that on a clean surface also.

16. Dump the solution out of both sensing cells by inverting the sonde over a suitable receptacle and give a slight shake to remove droplets within the cell. Take care not to spill solution on other parts of the instrument while doing this.

17. Recharge the ozonesonde with new solutions by adding 3.0 ml of fresh cathode solution to the cathode cell using a syringe reserved for this purpose then add 1.5 ml of anode solution to the anode chamber using a separate syringe reserved for anode solution. Note: The 2-minute wait period is not needed at this point because the ion bridge should already be saturated since the 3-7 days preparation

18. Replace the cathode cap by carefully sliding the long tube protruding out of the bottom of the cap over the Teflon rod protruding up from the bottom of the cell. Only when the tube is positioned correctly by the rod can the cap be pushed safely all the way into the top of the cell.

19. Reconnect the tube from the cathode cap to the pump outlet port and replace the anode cap.

20. Flush the syringes with distilled water before storing.

Note: From this point on the ozonesonde should always remain upright!

A-3.2 Connect the ozonesonde to the ozonizer test unit

21. Turn the ozonizer test unit and air pump on to allow it to warm up for 2-3 minutes before the ozonesonde performance checks are started.

22. Disconnect the shorting plug from the sensor leads. Connect the pump motor and sensor leads from the ozonesonde to the ozonizer test unit. This may require partially disconnecting the interface board first depending on the type of interface used. By means of a small piece of sandpaper or emery cloth, push fit one end of the air intake tube into the sonde pump inlet. The other end of the tube should be inserted a few centimeters into the no/low ozone port of the ozonizer/test unit.

23. Configure the ozonizer/test unit to produce ozone-free air (lamp off) and run the ECC pump motor for 10 minutes using the 12 VDC power supply in the ozonizer test unit. After the 10 minutes have elapsed, read the cell background current off the microammeter and record this value as ‘IB0’ on the checkout sheet to two digits after the decimal place.

A-3.3 Decay (response) test

24. With the sonde motor still running and the sonde continuing to sample air from the no/low ozone port, turn on the UV lamp on the ozonizer test unit and pull out the ozone control shield slightly. Make small adjustments to the position of the ozone control shield until a fairly steady current of 5μA is observed on the microammeter, then with a stopwatch start timing a 5 minute interval. Continue to make small adjustments to the ozone control shield as necessary to keep the sonde output near 5μA.

25. After 5 minutes have elapsed record the sonde current on the checkout sheet as the ‘initial current’ and then SIMULTANEOUSLY turn off the UV lamp and start the stopwatch.

26. Push the ozone control shield back into the ozonizer front panel and record the current indicated on the microammeter on to the checkout sheet after one half, one, two, three, five and 10 minutes have elapsed from the moment the UV lamp was turned off. After the 10 minutes have elapsed, read the cell background current off the microammeter and record this value as ‘IB1’ on the checkout sheet to two digits after the decimal place.

27. If the sonde current recorded at the one minute interval is less than 20% of the initial current (near 5 μA), the sonde has passed the decay test and can continue to the flow rate measurement. Otherwise corrective action is required.

A-3.4 Flowrate and final background measurement

29. After a successful ozonesonde response (decay) test, continue running the instrument on <u>ozone-free</u> air. Connect the soap bubble flow apparatus to the exhaust port of the cathode cell. Slowly squeeze the flow apparatus bulb until a steady column of soap bubbles are flowing up the glass burette tube. Continue until the entire glass column is thoroughly wet.

30. Once the inside walls of the glass column are clear of bubbles then record 5 flowrates (seconds per 100 cm^3) to the nearest hundredth of a second using a stopwatch. Record the room temperature and relative humidity on the checkout sheet and use these values to correct for the moistening effect on the pump flowrate measurement as shown in Section 3.2.4 by applying equations E-3-8 and E-3-9. Record the corrected pump flowrate and on the checkout sheet.

31. Turn OFF the 12 VDC SONDE MOTOR power and disconnect the bubble flow apparatus. Disconnect the sensor leads from the ozonizer/test unit and connect the leads to the sonde electronics interface board.

A-3.5 Prepare the ozonesonde box for flight

The following assumes a wet cell battery is being used. If this is not the case some of the following procedure will be slightly different.

32. Attach the meteorological radiosonde to the side of the polystyrene box with double stick and/or other tape but do not interfere with the front flap where the battery compartment and temperature sensor are located until the sensor and battery are in place for flight.

33. Connect all radiosonde and ozonesonde interface cables.

34. Place a small piece of double stick tape on the bottom of the pump battery and stick the battery to the base of the sonde frame. Check that the intake tube is firmly in the pump inlet port using a small piece of emery cloth to grasp the tubing. Now place the sonde inside the box with the intake tube resting in the angled slot in the box. Extend the leads from both the battery and the pump motor outside the box so power can be connected and disconnected once the lid is taped closed. Be sure that the battery lead wires do not interfere with the movement of the piston.

35. Before adjusting the temperature sensor to flight position touch firmly a large piece of metal to remove any static electricity you may be carrying (or wear a static-grounding bracelet). Open the radiosonde flap to release the temperature sensor and gently remove the sensor shield cap. Avoid excessive handling or touching of the sensitive sensor boom.

36. Attach an ozone filter, or provide a zero-ozone air flow, to the ozonesonde intake tube. Connect the 12 VDC SONDE MOTOR power from the ozonizer test unit to the pump and the 18 VDC power from the ozonizer test unit to the radiosonde power leads. Turn on power to perform a telemetry check with the data acquisition software. After the telemetry check, turn off all power to the sonde and disconnect the leads from the ozonizer test unit.

Note: Fill the balloon and prepare the load line before activating the wet cell!

A-3.6 Activate the wet batteries of radiosondes and prepare for launch

38. Cut open the foil pack containing the battery. Activate the battery by immersing in room temperature tap water in a small non-metallic container, taking care not to get the battery cell leads wet. Wait 2-4 minutes. Lightly shake out excess water. Carefully lift the temperature sensor and place the cell back into the battery compartment of the radiosonde with the wet cell leads extending outside the compartment.

39. Connect the wet cell battery leads to the radiosonde leads. Leads must be above the wet cell or outside the flap so moisture from the wet cell does not contact the connection. Lift the temperature sensor boom upward to close the flap. You may place a small piece of tape over flap to prevent it from opening during the flight. You may also add a supporting narrow piece of tape all the way around the radiosonde and Styrofoam box.

40. Perform a final visual check inside the sonde compartment of the box to be sure that the ozonesonde tubing is firmly in place and no wires or cables are interfering with the sonde piston pump.

41. Position the box lid and attach by wrapping two full lengths (about 100 cm) of tape all the way around the outside edges of the sonde to hold the lid and radiosonde support tape firmly in place.

42. Connect the intake tube to an ozone filter or set up to sample from a zero air source. Plug in power. Check that the data from the telemetry and signal strength is okay.

43. Allow the background to stabilize for 10 minutes while sampling **ozone-free** air. Record the final background as IB2 in the checkout sheet.

A-3.7 Surface ozone measurements at launch site

44. Carefully remove the sonde from the ozone filter and take the sonde package outside. Suspend the sonde about 1.5 meters above ground level. Run for 3 minutes to record surface ozone.

45. Record the surface pressure from a nearby standard ground measurement that is at approximately the same altitude level as the ozonesonde.
46. Record the number of minutes the sonde sampled surface air.

47. Check the incoming data once more. Then connect the ozonesonde to the balloon train.

A-3.8 Ready for launch

48. Check that the Radiosonde antenna is pointing down and the radiosonde temperature/humidity sensor boom is out and exposed to the air.

49. LAUNCH BALLOON

50. Record Local and UT date and time of launch on checkout sheet.

NOTE: Check the pump temperature when the balloon gets close to burst altitude. The pump temperature should be around 10-20 C at the end of the flight. If it is warmer than about 20 C then you may need to bore in ventilation holes in the side of the Styrofoam box. If the pump temperature is cooler than 5 to 10 C then the instrument and sensor cell may be getting too cold and will require a small battery heater placed next to the sonde frame.

A-4 Balloon Train and Launching

The ozonesonde instrument is carried aloft by a rubber balloon filled with hydrogen or helium. In polar regions where temperatures < minus 70deg.C are encountered, plastic 10K to 19K, 0.3 mil balloons should be used. The ascent rate of the ozonesonde and balloon burst altitude are related to the weight of the entire ozonesonde balloon train, the amount of lifting gas used to inflate the balloon, balloon size, and environmental conditions (temperature, stability, and sunlight).

The typical rise rate ranges from 250-350 meters per minute, with burst occurring between 28 and 35 km altitude.

The typical balloon train consists of:

1. The ozonesonde instrument.
2. A payout reel (ratchet- type or unwinder with approximately 30-40 meters of string.
3. A parachute to slow the descent after balloon burst.
4. Rubber balloon (typical sizes are 600, 800, 1000, 1200, and 1500 grams).

The proper amount of lifting gas for inflation of the balloon should be approximately 35-50% in excess of the weight of the entire ozonesonde balloon package and train weight (ozonesonde + balloon + payout reel, etc.). This can be adjusted depending on local conditions and experience with previous rise rates and burst altitudes attained. The lifting gas volume needed is determined by two methods

1. The volume of gas is measured by a meter or the pressure drop measured from the source lifting gas tank pressure gauge.

2. A dummy weight (weigh-off weight) is used. The lifting gas inflates the balloon until the dummy weight is just lifted (floated) off the floor. This is difficult if done outside under windy conditions.

An example of the dummy weight calculation using 40% lift is given below:

Weight of ozonesonde + radiosonde package = 800 grams
Weight of payout reel + string = 130 grams
Weight of parachute = 80 grams
Total Weight of Package = 1010 grams
+
Weight of balloon = 1200 grams
Total Weight of entire sonde balloon train = 2210 grams

Dummy weight = (Total Weight + 40%) - (weight of balloon)
= 2210 x 1.4 - (1200) = 3094 – 1200 = 1894 grams (~1800 – 2000 grams)

Each station may have different routines for balloon train preparation and launching. Here are some general suggestions.

- Always check that the payout reel or unwinder will not jam and will release the line in a steady, slow manner. A typical ratchet payout reel will have one loop of the string going around a cylindrical bar to slow the speed of the line release.
- The typical weather radiosonde unwinder is designed for the small weight of a single radiosonde and should not be used with the ozonesonde package, which typically weighs up to 1 kg. The extra weight could draw out string from the unwinder at a faster rate than the balloon rise rate, resulting in a ground crash at launch.
- Remove rings, watches or other objects that may scratch the rubber balloon during inflating and handling.
- The balloon can be launched by one person when winds are less than about 15-20 knots. It is best to hold the rubber neck of the balloon and top of parachute in one hand and the sonde and payout reel in the other when carrying the ozonesonde out of the inflation facility. Slowly let the string and chute up until line is taut at the payout reel and sonde. If the wind is brisk you may have to run with the wind for a few meters just before release.
- Be careful not to make contact with the radiosonde temperature sensor boom with your hands, arms, or string while handling the balloon train during launch.

Web site for miscellaneous radiosonde or ozonesonde preparations:

http://www.ua.nws.noaa.gov/preparing_for_vaisala_rs80.htm

A-5 Trouble Shooting

(a) No data coming in

Loose or poor connections from the antenna to the receiver are the most common problem. Check all connections.

Make sure Receiver is adjusted properly for band tuned to the strongest signal and that the attenuate button has not been turned on.

(b) High Background (greater than about 0.10 microamps)

Change both cathode and anode solutions as outlined in the day of preparation procedure. Run on filtered air for several minutes. If the background is still high then try ozonesonde on another source of zero-ozone air or a different filter (see Section A-6). If the background is still high consider preparing another ozonesonde.

(c) Interference from other transmitters in the 400 to 406 MHz range

You may have to tune the radiosonde frequency up or down from 403 MHz to a cleaner region in the allowed 400.15 to 406 MHz range to shift away from other possible signals.

(d) Pump temperature does not show a typical value or shows no value

Check that the pump temperature thermistor is plugged into the interface board and that there are no broken wires.

(e) Pump temperature is too cold or too warm (outside a range of 5 to 30 ^{o}C)

The pump temperature should be between 25-35 C at launch and 5-20 C at burst altitude.

If pump temperature at burst has been greater than 20 C:

(a) Make one or two small ventilation holes (~1/2 cm diameter) in the side of the box.

If pump temperature at burst altitude is less than 10 C:

(a) Add a sealed, non-leaking, air-free water bag or a resistor heater and battery next to the sonde frame.
(b) Make sure the lid is sealed well
(c) Be sure that the starting pump temperature is around 29 to 35 C or warmer.

A-6 Alternative Sources of Filtered or Zero Air

Filtered or zero-ozone air is used during several stages of the ozonesonde conditioning and performance checks. It is important to use high quality ozone-free air, especially during the sensor background measurements. The ozonizer/test unit provides a very good source of zero-ozone air. When the test unit air pump is switched on, ambient air is pumped through a particulate filter and chemical cartridge at approximately 1 liter per minute. The series of cartridges remove nearly all aerosols, dust, ozone, and other trace gases that may affect the ozonesonde sensor. The cartridges are considered to be good for several years if the test unit is used in a clean, relatively dry, non-smoking room. However, other zero-ozone air sources should be considered if the ECC ozonesonde backgrounds have been drifting higher than normal compared to previous flight preparations. This may occur, for example, at tropical sites where the test unit exposure to high humidity air may eventually reduce the effectiveness of the filter cartridges.

In this case other zero-ozone options that may be considered are 1) external pump and canister filters 2) zero-air cylinders.

(1) The external pump and canister filters setup shown below consists of a charcoal column used in series with a calcium sulfate (purchased commercially as Drierite) desiccant column that extracts water vapor to give a dry zero-ozone source of air. The output flow rate should be at least 0.6 liters/min, which is about three times the flowrate of the ozonesonde (~ 215 ml/min). Higher flow through the desiccant column is normal but will require more frequent regeneration of the Drierite desiccant. As the indicating Drierite granules absorb moisture they turn pink in color. Regeneration is done by spreading out the granules onto a tray and drying in a warm (~200 C) oven for 1 to 2 hours.

Each of the columns are approximately 25 to 30 cm in height. An aluminum grating plate and fiber filters are used to hold the desiccant or charcoal granules in place and filter out any smaller particles before the output flow.

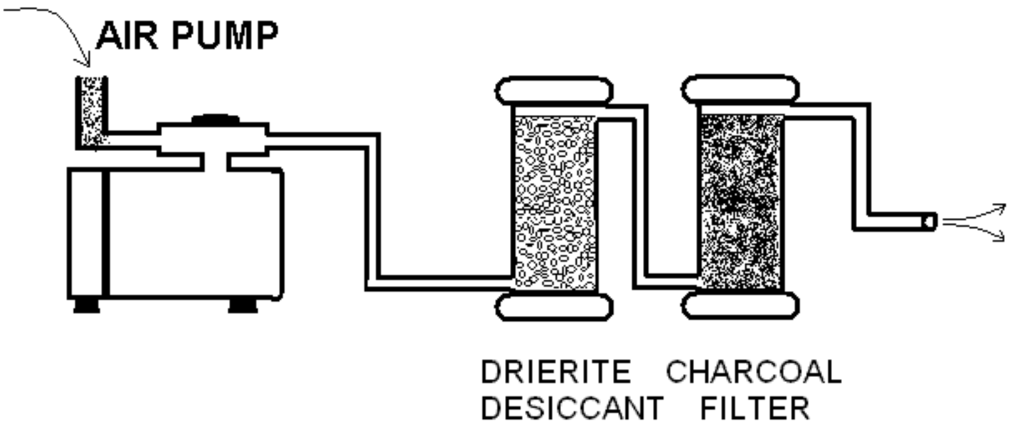

Figure A-2: Set up of air purification

(2) The Zero-Air Cylinder setup is shown below. Zero-air tanks can be obtained from most gas suppliers (tanks may be rented or purchased). Additional items required are a properly sized pressure regulator and a gas flow meter.

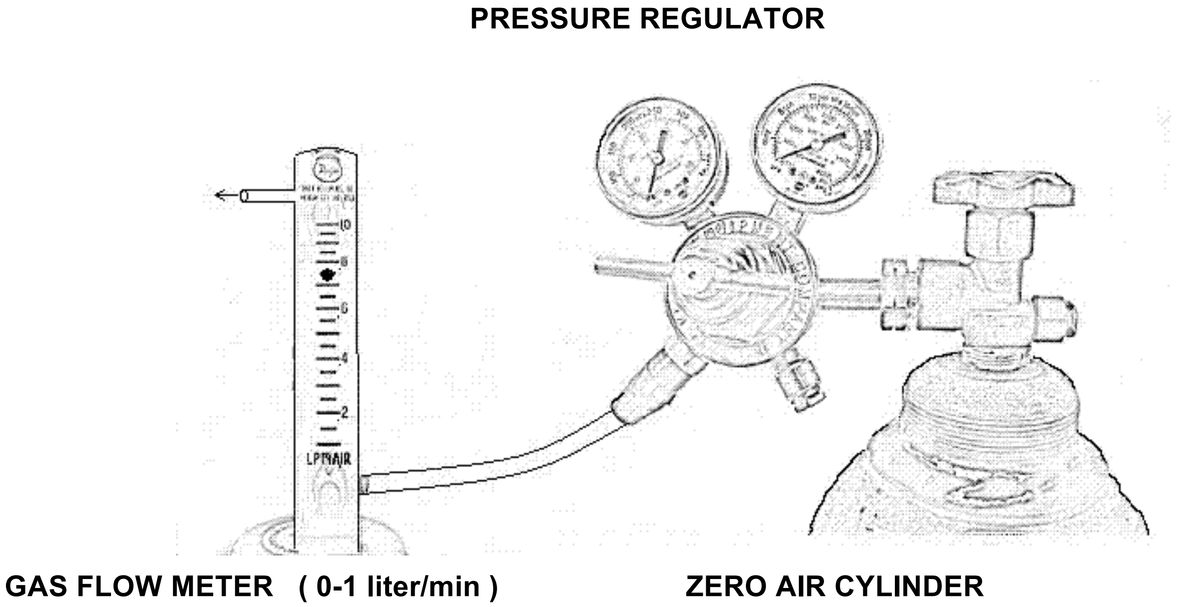

Figure A-3: Zero-air supply from storage cylinder

The tanks can be filled (~ 2000 psi, or 13,800 KiloPascals) with:

(1) Standard Zero Air which typically has zero ozone, 3ppm water, and a maximum of 0.5 ppm hydrocarbons (HC).

(2) Ultra High Purity (UHP) zero air. UHP zero air is the highest grade zero air but not needed for ECC background use. This air (< 0.1PPM HC) goes through an additional cleaning process to take out a little extra water vapor and HC, therefore it may cost approximately twice as much as standard zero air.

The high cost of shipping pressurized cylinders is one of the only disadvantages for this method. Therefore, extra care must be used to conserve the gas. One option is to only use the zero air for 3-5 minutes when obtaining the final ozone background. Also be sure to immediately close the cylinder valve and turn the gas flow off when finished.

A-7 Check List “Ozonesonde Conditioning And Pre-Flight Preparation”

OZONE SONDE CONDITIONING AND PRE-FLIGHT PREPARATIONS

3-7 Days Prior to Launch

Date ________________________ Ozone Unit Number __________________ Initials ___________

Initial Pump Current ____________ mA (~< 100 mA)
Pump Head Pressure ____________ psi (~>10 psi)
Pump Suction ____________ inches Hg (~< 20 in Hg)
Condition with High Ozone for 30 min (tubing, pump, cathode chamber) [ ]
Condition with Zero Ozone (filter) for 5 min [ ]
Fill with Cathode Solution (3 ml). Wait 2 min [ ]
Fill with Anode Solution (1.5 ml) [ ]
Condition with Zero Ozone for 10 min [ ]
Run on high ozone (5 µA) for 10 min [ ]
Ozone free air for 10 min. Check that O$_3$ decreases by 70-80% in 1 min [ ]
Background current may be 0.2 - 0.5 µA at this time. It will decrease in the next days
Add 3 ml to cathode. Short ECC-cell Leads. Replace in Plastic Storage Bag [ ]

---

1 - 24 hours prior to flight (multiple columns/rows allow for multiple tests of same ozonesonde)

Date	____________	_____________	_____________
Initials	____________	_____________	_____________
Rinse Cathode and Anode cells	[ ]	[ ]	[ ]
Replace Cathode (3 ml)	[ ]	[ ]	[ ]
Replace Anode (1.5 ml)	[ ]	[ ]	[ ]
Attach cell leads to ozone generator	[ ]	[ ]	[ ]
Ozone free air on pump intake	[ ]	[ ]	[ ]
Pump motor current (~<100 mA)	____________	_____________	____________mA
Background /~time to bkg	____________	_____________	___________µA

Replace solutions if background is ~≥0.10 µA (~0.35 mPa).

Moderate ozone (~5 µA) for 10 minutes	[ ]	[ ]	[ ]

Switch to ozone free air and record (µA) at:

0.0	0.5	1	3	5	10 min	
_________	_________	_________	_________	_________	_________	(1)
_________	_________	_________	_________	_________	_________	(2)
_________	_________	_________	_________	_________	_________	(3)

Flow rate (ml min$^{-1)}$	___________	_____________	_____________

Vaisala attached, ozonesonde leads attached with correct polarity. Vaisala #_____________
Insert heater, ozonesonde, batteries, make all connections, and

Check telemetry	[ ]	[ ]	[ ]
Record P/T/RH	___________	_____________	_____________
Ozone Background in lab:	___________	_____________	_____________ hex/mPa
Background before release:	____________	_____________	_____________ hex/mPa
Surface ozone before release:	____________	_____________	_____________ hex/mPa
Ozone pump temp:	___________	_____________	_____________°C

Twist heater leads together if using a battery to heat ozone pump.
Straighten Antenna

~ Surface winds at launch:	____________	_____________	_____________ knots

Flight Number: Flight Date: Vaisala #

ANNEX B

Standard Operating Procedures For Brewer/Mast Ozonesondes:

A practical guidance

Lead author
Hans Claude
(Meteorological Observatory Hohenpeissenberg, Germany)

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B-1 INTRODUCTION

The Brewer/Mast ozonesonde (Figure 1) is based on earlier types by Brewer and Milford (1960). Using the electrochemical oxidation of potassium iodide by ozone in an aqueous solution, they had developed a system that allows continuous ozone measurements by high altitude balloon-soundings up to 30km. The Brewer/Mast sonde and accessories are manufactured and sold commercially by Mast Keystone in Reno, Nevada, USA. The most recent version is the type 730-10 (Figure 1), which is manufactured since 1997 in Costa Rica.

Manufacturer's Addresses

Mast Keystone Inc.
2200 Dickerson Road
Reno, Nevada 89503
Tel: (800) 806-6569
Fax: (775) 324-5375
sales@mastdev.com

Mast Keystone Inc.
P.O. Box 16-5750
Bagaces, GTE
Costa Rica
Phone: + 506 283 2839

The main components of the sonde are a reaction chamber (bubbler), an air-pump driven by an electric motor, signal conditioning electronics and a power supply. All parts are protected in a styrofoam box giving good thermal insulation to maintain an internal operating temperature above 0ºC. In order to transfer the ozone signal to a ground receiver and to record meteorological data, the ozonesonde has to be connected to a suitable meteorological radiosonde.

At Hohenpeißenberg the Brewer/Mast ozonesonde is coupled via RSA92-2 interface adapter card to the Vaisala-Radiosonde RS92-SGPD. However, it can also be connected to other radiosonde types.

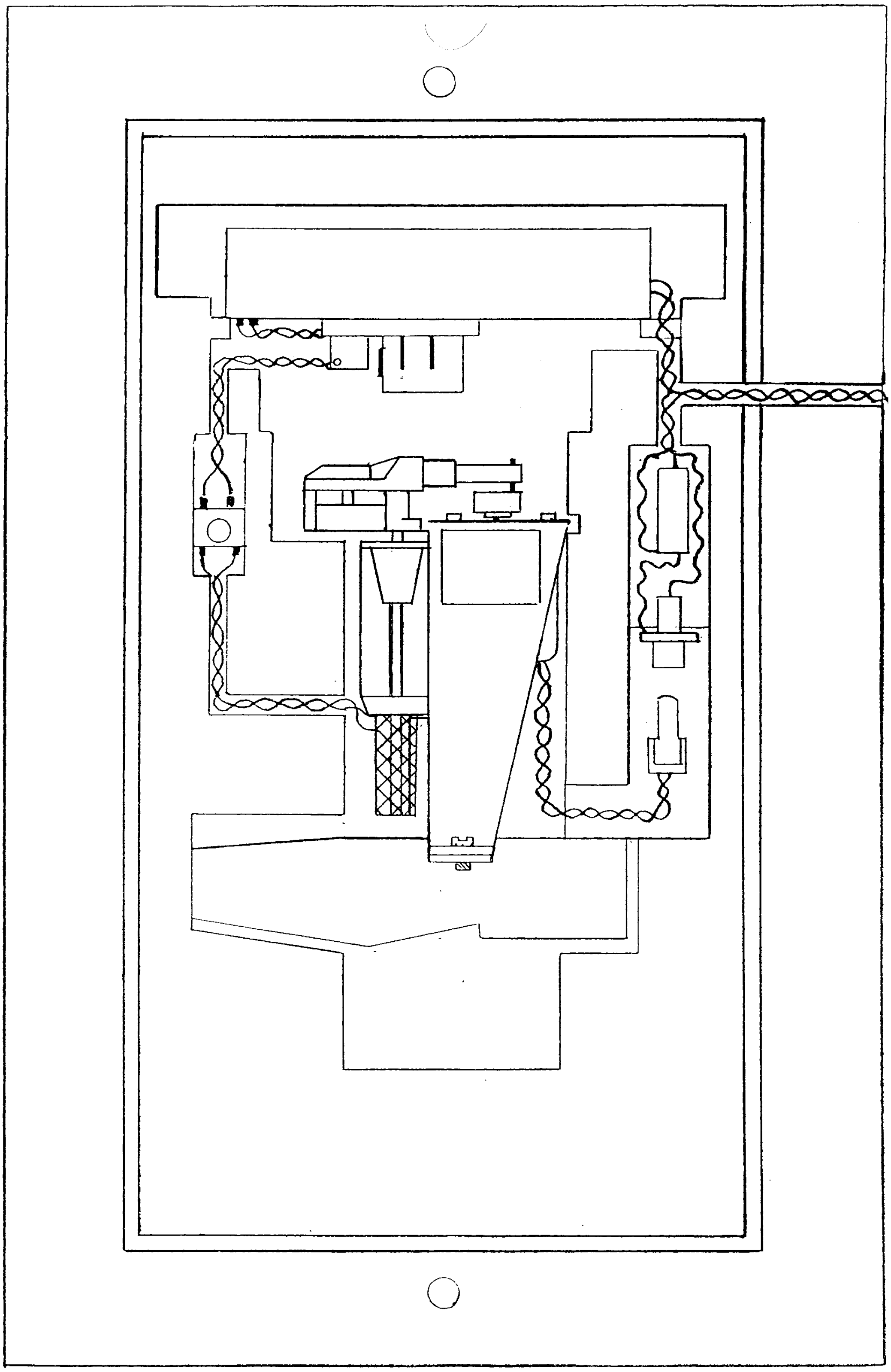

Figure 1 - Cross-section of styrofoam box containing the Brewer Mast sensor with pump and interface card

B-2 DESCRIPTION OF THE BREWER/MAST SONDE

B-2.1 Principle of operation

Measurement principle of the Brewer/Mast sonde is the electrochemical oxidation of potassium iodide. At the platinum cathode of the bubbler, iodine gets oxidised:

$I_2 + 2\ e^- <> 2\ I^-$

at the silver wire anode, on the other hand, the silver gets oxidised by the iodide:

$2I^- + 2\ Ag <> AgI + 2\ e^-$

Since silveriodide is stable it is bound to the anode and not available for further reactions.

If a voltage of 410 mV is applied between the platinum mesh cathode and the silver wire anode the polarisation voltage between the two is compensated. No electrons flow between anode and cathode and iodine and iodide concentration in the cell reach an electrochemical equilibrium. If an ozone molecule enters the solution, it can react with the iodide according to

$O_3 + 2\ H^+ + 2J^- > J_2 + H_2O + O_2$

This displaces the equilibrium and 2 electrons flow until equilibrium is restored. In a complete reaction cycle, two electrons are released per ozone molecule. Registering the current can thus provide an absolute measure of the amount of ozone reacting in the bubbler per unit time.

N ozone molecules give a charge $Q = N \cdot 2e$. Using the ideal gas law ($p \cdot V = N \cdot k \cdot T$, where p is the partial pressure, V the volume, N the number of molecules, k the Boltzmann constant and T the absolute Temperature) it follows that

$pV = Q \cdot k \cdot T/(2e)$

or as $Q = I \cdot t$ where I is the measured current and t the time:

$p = I \cdot k \cdot T/(2e) \cdot t/V$

or

$p = 4.31 \cdot 10^{-3}\ I \cdot T \cdot t/V$

where p is the ozone partial pressure (in nbar), I is the measured current (in µA), T is the pump temperature (in K) and t/V is the time in seconds which is needed to pump a volume V of air (100ml) through the cell.

The current created by ozone in the bubbler is of the order of a few µA. The radiosonde interface converts the current to a signal that is passed to the radiosonde. The radiosonde transfers the ozone signal along with meteorological parameters to the groundstation where all signals are decoded and recorded on line.

B-2.2 Bubbler and pump unit

The reaction chamber (bubbler) is made out of plexi-glass. It contains a cylindrical platinum mesh cathode of about 6 cm^2 and a thin silver wire as the anode. Both are mounted so that no metallic contact between them is possible. The bubbler is filled with 2 ml of neutrally buffered 0.1 % solution of potassium iodide in water. An air pump is mounted right next to the bubbler. The pump is driven by a constant speed electrical motor (e.g. MABUCHI, EG-530AD-9F, 9 VDC (2400) CW) running at 2400 rpm for input voltages between 8.7 and 15 Volts. Through short PTFE hoses the pump transfers outside air to the bottom of the bubbler. There, small bubbles pass along the platinum mesh and rise through the solution for a length of about 2.5 cm.

B-2.3 Powersupply for ozone- and radiosonde

The Brewer/Mast ozonesonde requires power for the pump-motor and to sustain a bias voltage between anode and cathode of the reaction chamber. Usually, suitable water-activated batteries are delivered with the Brewer/Mast ozonesonde. In flight, these batteries are housed in a special battery compartment on the outside of the styrofoam box.

As an economic, modern alternative, the ozonesonde can also be powered by a battery pack consisting of 4 Lithium cells of 3 Volts each (e.g. Panasonic Lithium Battery BR-2/3). The main requirement is that the batteries can supply a stable output not lower than 9 Volts for at least 2 hours, and at temperatures that can go below 0°C. These batteries should be mounted for flight within the styrofoam box of the ozonesonde.

In connection with the Vaisala-Radiosonde RS92-SGPD, the Vaisala RSA92-2 interface supplies the necessary 410 mV bias voltage for the bubbler. Alternatively 410mV can be supplied by a miniature Mercury-Oxide 1.35 V cell within the original Brewer/Mast electronics interface (black box).

The radiosonde is separately powered by batteries packed and delivered by Vaisala. This battery-pack gives a stable 9-Volt power supply for at least 2 hours.

B-2.4 Weights

{PRIVATE }**Vaisala RS92-AGP Radiosonde**	
Radiosonde, without battery pack	98g
radiosonde with battery pack	142g
RSA 92-2Vaisala interface to Brewer/Mast	15g
total radiosonde + interface	**255 g**
Brewer/Mast 730-10 ozonesonde	
pump, motor, bubbler, solution	120g
ozonesonde battery pack, 3V Lithium	70g
styrofoam enclosure	300g
accessories (water-pads, capacitor, request for return letter)	100g
total ozonesonde	**590g**
flight accessories	
parachute	125 g
roll off winch	120 g
Latex balloon	
total payload	**1090g**

Note: by changing to the RS92-SGPD radiosonde, the payload weight has become smaller. In order to keep the ascent velocity comparable to before (300 to 350 m/minute) the buoyancy of the balloon (e.g. a TOTEX TX 1500) was reduced to 2750g.

B-2.5 Dimensions

Vaisala radiosonde (rectangular: length, width, height)	95, 55, 150 mm
Brewer/Mast ozonesonde (cylindrical: diameter, height)	225, 340 mm

B-3 PREPARATION OF THE BREWER/MAST SONDE

When working with the Brewer/Mast sonde, extreme cleanliness is of paramount importance. The procedure followed at Hohenpeissenberg differs substantially from the one recommended by Mast Keystone in their 1976 manual. Strict adherence to the procedure is especially important for retrieved used sondes which can be used again after refurbishing. As experience shows, the entire procedure is required for new sondes as well.

B-3.1 Unpacking

The *radiosonde* is delivered in an air-tight package complete with all accessories, including battery and unwinder for the radiosonde alone. Radiosonde type, serial number and frequency are also marked on the package. At Hohenpeißenberg, this unwinder is not used, instead we use a stable aluminum winch manufactured by Firma Dr. Graw, Messgeräte GmbH & Co, Muggenhofer Straße 95, 90429 Nürnberg, http://www.graw.de/. Usually the sonde is ready for launch as delivered and the sonde package is only opened during launch preparation.

The *RSA92-2 ozonesonde interface* is packaged in the same way. Another unwinder is included, as well as information about the individual RSA92-2 calibration values. At Hohenpeissenberg these reference values are entered into a script-file on the data acquisition computer used for the sounding prior to the actual launch preparation. This means that the package has to be opened.

When delivered, the *Brewer/Mast ozonesonde* comes with all accessory parts and a calibration data-sheet containing information about sonde type, serial number, pump performance and a sensor calibration plot. Because the performance of the bubbler depends a lot on preparation, the value of the calibration plot is doubtful and should not be relied on. A couple of small parts can be found in a plastic bag in the external battery compartment. When opening the styrofoam enclosure, all parts should stay in the rear half.

B-3.2 Preparation of sensing solution

The chemicals required for preparation of the potassium iodide solution are usually included when a batch of sondes is delivered by Mast/Keystone. Standard practice at Hohenpeissenberg is to set-up a highly concentrated (1 %) mother solution from which the actual 0.1 % solution is drawn. When stored in the dark, the mother solution remains stable for weeks, whereas the reaction solution should be used fairly soon.

Mother solution:

Fill about two thirds of a 100 ml bottle with bi-distilled water. Then add the following substances in sequence. After each substance shake the bottle thoroughly, until everything is completely dissolved:

1.888 g $Na_2HPO_4 \times 7\ H_2O$ or 2.522 g $Na_2HPO_4 \times 12\ H_2O$	di-sodiumhydrogen phosphate
1.150 g $NaH_2PO_4 \times H_2O$	sodium-dihydrogen phosphate
1.000 g KI	potassium iodide

Finally, the bottle is filled to 100 ml with bi-distilled water.

Reaction solution:

In a plastic bottle, 5 ml of mother solution and 45 ml of bi-distilled water are combined and mixed very well.

Because these solutions decompose photochemically, both should only be exposed to light for a very short time.

B-3.3 Cleaning of bubbler, anode and cathode

For cleaning, the bubbler has to be carefully disassembled (Figure 2). First, loosen the teflon ring and take it out. Then remove the entire platinum mesh, using only plastic or ceramic tweezers. Pay special attention not to break the fine and brittle connecting wire. If the wire does break, it can only be repaired by point-welding.

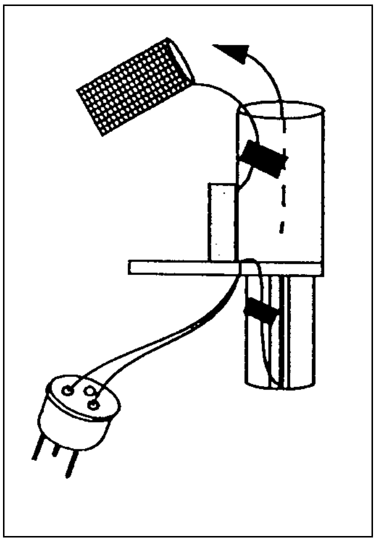

Figure 2 - Bubbler with the cylindrical platinum mesh removed (old plug)

The procedure for cleaning the silver anode was changed in September 1993. Before, the anode was cleaned using a commercial silver cleaner and a brush. Since, a basic potassium cyanide solution, consisting of 400 mg NaOH and 650 mg KCN in 100 ml H_2O, is used for cleaning. This procedure removes silveriodide very effectively, which is otherwise hard to dissolve. Potassium cyanide, however, is highly toxic. The required precautions have to be taken! After use, the potassium cyanide solution has to be disposed according to current safety regulations. Use protective gloves (e.g. latex-gloves) when working with the cyanide. Dispose them according to current safety regulations afterwards. Intermediate storage of used potassium cyanide in a special container filled with chlorine-lime (bleach-powder) is possible.

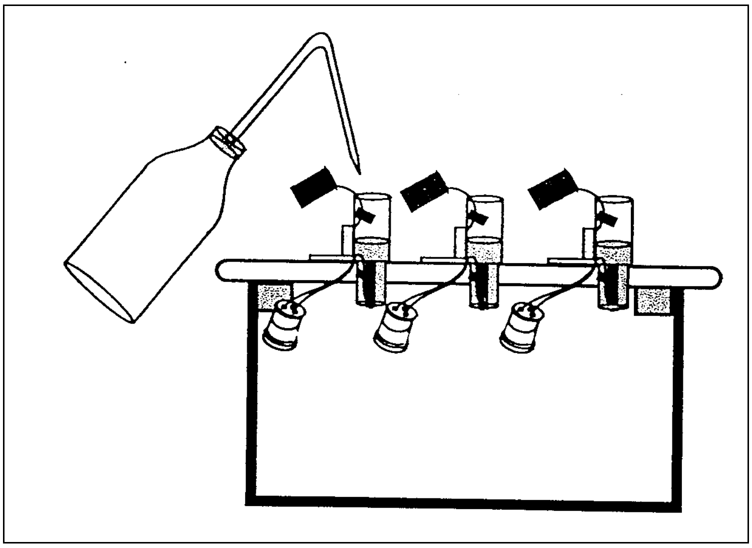

Figure 3 - Rack for a safe foothold of the bubblers during flushing

The silver anode remains in the bubbler for cleaning. First, fill the bubbler with the potassium cyanide solution until the silver wire is covered (Figure 3). Then close up the bubbler with a teflon-plug. Everything is left sitting for a couple of minutes, so that potassium cyanide solution can dissolve dirt and silvercompounds from the surface of the wire. If necessary, tilt the bubbler or shake it. Afterwards, pour the potassium cyanide solution out of the bubbler. The silver wire should be clean and give a metallic shine. Wash bubbler and silver wire several times with distilled water. Dispose of this water in the same way as the cyanide solution. Cleaning of the anode is now finished.

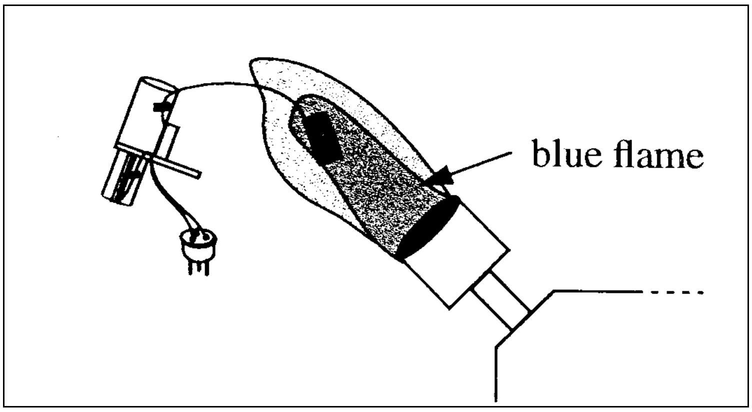

Figure 4 - Heating of the platinum mesh in the hot spot (blue) of a gas-flame

Over a teflon-form the platinum cathode mesh is brought back into its original cylindrical shape. Extending wires are removed with a small wire cutter. Heat the platinum mesh over a smoke-free and colourless Bunsen-burner flame (Butane/Propane gasmix) until it glows red (Figure 4). Take special care not to break the connecting wire and not to melt the teflon ring. Note: Also the platinum mesh can melt in a very hot flame.

Next, fill an ultra-sound cleaning bath with distilled water and some ultrasound cleaner (e.g. RBS 35, Carl Roth, Karlsruhe, http://www.carl-roth.de/website/en-de/carl-roth_index.jsp). Put a number of bubblers and their removed platinum meshes into the bath. Be careful not to let the meshes entangle and not to break them. Also, no air should be trapped in the bubblers, because otherwise these areas will not be cleaned. Keep the connectors coming from the bubblers outside of the bath and make sure they do not get wet. Set heating for the water/RBS bath to 50° C and timer to 15 minutes. Ultrasound cleaning ends after 15 minutes. The heating has to be turned off. After removing bubblers and platinum cathodes the cleaning solution is disposed of.

This procedure is repeated three more times, however, only distilled water and no RBS solution are used. This is necessary to remove all traces of RBS from bubblers and platinum cathodes.

Finally, tilt the bubblers in order to remove remaining water drops. Bubblers and platinum meshes are then dried in an oven for 12 to 18 hours at 50° C.

When completely dry, the platinum mesh is reinserted into the bubbler using plastic or ceramic tweezers. It has to be centered in the middle of the bubbler. Using an Ohm-meter, check that platinum cathode and silver anode are not electrically connected. At the same time, check the connections between white wire and silver anode, between red wire and platinum cathode, and with the respective pins on the connector-plug.

Until they are needed, the bubblers can be stored in the dark in a well sealed plastic box (e.g. tupperware). Before use, they have to be filled with potassium iodide solution, closed with a teflon plug and stored in the dark for at least 24 hours.

B-3.4 Cleaning of the pump

First check the length of the tube leading from the pump into the bubbler. It should be 62mm (see figure 5). If necessary, the tube has to be shortened using clean side cutters. If the tube is too long, proper airflow from the pump through the bubbler is not guaranteed, because the tube will not fit correctly on the small holding pin on the bottom of the bubbler and may even be blocked.

Next, fill the ultrasound-bath (or another absolutely clean container) with distilled water and RBS cleaning fluid and heat the solution to 50°C. When using the ultrasound-bath, only use the heating, but do not turn on the ultrasound. Mount the pump using the clamp of a laboratory-holder or something similar, so that the intake tube is in the heated cleaning solution. Then the pump is run at 4 – 4.5 Volts for about 10 minutes with the cleaning solution recirculated through the ultrasound-bath or container. To avoid destroying the pump cylinder, 5 Volts must not be exceeded. If the black crankshaft comes off the motor shaft the motor has to be exchanged. Try to glue the black crankshaft to the shaft of the exchanged motor.

After about 10 minutes, the pump is flushed by pumping distilled water from another container. This way, all residues of the RBS solution should be removed. Finally, to remove as much water from the pump as possible, the intake is connected to the ozone generator, or to the zero-filter. In no case ambient air should be pumped in, because it can contain ozone destroying contaminants which might be deposited in the pump.

Now the pumps can be disassembled. Make sure to keep track of which piston belongs to which pump. It is best to connect piston, pump and bubbler attachment with a thin nylon cable. Do not use wire or other metals. Motor, bolts and mounts can be put aside.

After cleaning the ultrasound-bath with distilled water (to remove residue from before) it is refilled with distilled water and some RBS. Make sure that no air is left in the tubes when putting the pumps into the cleaning solution, otherwise these areas will not be cleaned. The ultrasound-bath is run for about 15 minutes at 50°C. This procedure is repeated three more times, however, only distilled water is used. Shake remaining water from the pumps and dry all parts for 6 to 10 hours at 50°C in the oven.

When completely dry, the pumps are reassembled. Be careful not to touch the tube that goes from the pump into the bubbler. Until testing for their flow rate, the pumps are stored in well sealed plastic boxes in the dark.

B-3.5 Oiling of the pump

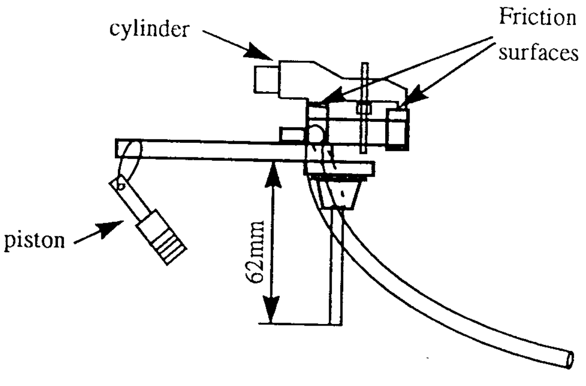

Figure 5 - Pump and air-inlet device with removed piston and motor (not shown)

Oiling of the pump is of great importance for the Brewer/Mast pumps. Before the pump can be run, it has to be oiled, however, only with a thin film of oil. Take the pump out of the storage container, remove the piston and expose the surfaces with the steering slits (Figure 5). Take a piece of lint free tissue or cloth (Kleenex or optic cleaning tissue) and put a small drop of oil on it. Wipe the piston and the steering slit surfaces with the lightly oiled tissue. After oiling reassemble the pump.

Until early 1994, special piston oil from Mast/Keystone was used. Since then high quality sewing machine oil (e.g. Pfaff) is used. This oil is resinfree, odourless and works at low temperatures.

B-3.6 Measuring the flow rate

Mount the assembled pump (e.g. in a laboratory holder) and attach the intake tube to an ozone source. At Hohenpeissenberg the ozone source ("ozone box") is an airtight box with an UV-lamp inside that generates ozone. Connect the pump to a power supply with 12 V (maximum 15 V). To insure the right polarity (+/-), it is recommended to prepare a cable with a special connector. This will guarantee the right direction of rotation of the pump motor.

Before the flow rate test, the pump is "dry-activated" by pumping ozone rich air (about 1 ppm) for at least 15 minutes. This makes sure that on the one hand the pump is run in properly, on the other hand, remaining contamination is oxidized. In our experience, this "dry activation" process will have a positive effect on the performance of the ozonesonde later.

After 15 minutes the pump should be running uniformly and the flowrate can be measured with a burette. It is important to have a precise measurement of the flow-rate, as it directly enters the calculation of the ozone partial pressure. In order to correctly simulate the backpressure encountered by the pump during flight, a bubbler-like container is attached to the exhaust side of the pump. This container is filled with distilled water up to a height of 2 cm. The other side of this container is connected to a 100 ml burette with a small rubber balloon full of soap-water at its bottom.

If you intend to check the efficiency of the entire pump-bubbler assembly with a calibrated ozone generator later, you should now connect the pump intake to a zero-filter. Otherwise, ozone can accumulate in the pump and lead to wrong results in the efficiency test of the entire system.

When everything is connected and running, create a soap bubble by pushing the rubber balloon. The airflow from the pump moves this bubble through the burette. Using a stop watch, note down the time the soap-bubble takes to cover the 100 ml volume, which gives a direct measure of the pump flow rate. This procedure should be repeated 5 times. The standard deviation of the measurements should be below 0.2 seconds. From the 5 results the longest and shortest times are not considered. The average of the other 3 results is used as the flowrate of the pump. The result is noted on the calibration sheet of the pump. Typically, values lie between 24.0 and 30.0 seconds. Measure and note also down the current drawn by the pump motor, which typically is approximately 100mA.

Recent tests have shown that even after running for 4 hours the flowrate of the pumps does not change considerably.

B-4 TEST OF THE ENTIRE PUMP/BUBBLER SYSTEM

To avoid surprises during launch preparation at Hohenpeissenberg, the ozone sensors are tested with a calibrated ozone generator. As mentioned, the bubbler should have been filled with KI solution at least 24 hours before this test. Before starting the test, check the potential between anode and cathode with a multimeter. Normally, this voltage is above 410 mV. A smaller voltage indicates contamination, dirt or a poor KI solution. With such bubblers, the sonde responds to ozone changes only very sluggishly and often registers only 70 % and less of the true ozone partial pressure. Such a bad bubbler should not be launched and has to be cleaned again.

If the voltage is alright, the real test can begin. Connect the bubbler to the so called lab-electronics. This is a device for conversion of the bubbler current (a few microamps) to a DC voltage (0 to 5 V), which can easily be measured by a multimeter. The lab-electronics also supplies the -410 mV bias voltage needed for compensation of the anode - cathode potential difference.

The ozone partial pressure p (in nbar), measured by the sonde, can be derived from the output voltage of the lab-electronics:

$p = K \cdot V/t \cdot I$

Here V/t is the pump flow-rate (in 100 ml/s), I is the current (in µA) or voltage (in V) registered by the lab-electronics, and K=1.293 is a calibration constant which assumes a pump temperature of 300 K.

For the first test the sonde is connected to a zero ozone filter. This is a black carbon filter which does not allow ozone to pass. Attach the intake tube of the pump to this filter. The voltage from the lab-electronics should drop rapidly and ozone (derived by the above formula) should be below 3.5 nbar. At this point check the bias voltage supplied from the lab-electronics. It should be 410 ± 10 mV.

In the next test the sonde is connected to the calibrated ozone generator. For an input of 100 nbar ozone, the sonde should register at least 90 nbar. Sondes with lower registered ozone should be recleaned and eventually rejected. The registered values are noted on the sonde's calibration sheet. They serve as a reference for the performance in flight, but are not used to calibrate the ozone profile determined in flight.

This ends the preparation of the ozonesonde consisting of intake and exhaust tubes, pump, bubbler, anode, cathode and solution. During preparation, it helps to mark the individual pieces, so that it is possible to keep the same pump/bubbler system together.

B-5 STORAGE OF THE PREPARED SENSORS

Until the day of flight, pump and bubbler are taken apart and stored separately. The bubbler is filled with KI sensing solution and closed with a teflon-plug. It is stored in the dark. After a short storage (1 to 3 days) it can even be used with the same solution in flight.

Until flight, the pump is stored in an appropriate ozone box as it is shown in Figure 6. The ozone mixing ratio within this box should amount to approx. 1 ppm. Just before launch the flowrate of the pump is checked again and updated if necessary.

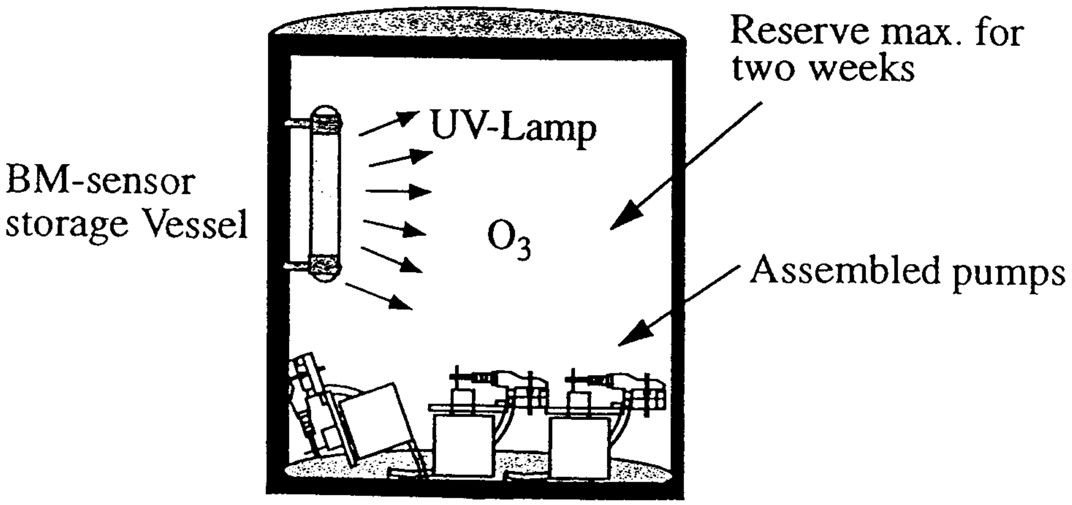

Figure 6 - Ozone box for safekeeping the entire pump device

B-6 FINAL PRE-FLIGHT PREPARATION ON DAY OF FLIGHT

B-6.1 In the laboratory

1. First of all make a initial pump test. Take 5 measurements according to section 3.7, discard the highest and lowest value, note down the mean out of the remaining value for the evaluation. Use purified air for the test.

2. Check again the polarisation voltage at the bubbler leads. It has to exceed 410mV. Pour the KI-solution out of the bubbler.

3. Assemble the bubbler with the pump device carefully. Pay special attention that the inner teflon tube fits well on the pin at the bottom of the bubbler. Place the pump/bubbler unit into its compartment of the corresponding half of the styrofoam box.

4. Place also the battery pack into its compartment. Insure the right polarity (+/-) of the leads and plugs. Install the interface and couple the ozonesonde with the radiosonde.

5. Turn on the radiosonde telemetry system. First, check the correct function of interface, radiosonde and receiving system with a stable current source instead of the bubbler. Set the current on 6microamps. Is this signal transmitted and recorded correctly by the system? Up to this point the ozonesonde is powered by the laboratory power supply. Now switch to the internal battery pack. Then make a final check of the entire system at the ozone generator and with purified air free of ozone to guarantee a proper function of the entire system.

6. If everything is fine, mount the second half of the styrofoam box. Before affixing tapes, do not forget a sling around the upper wooden pin for attaching the balloon train at the launch. Make all the devices ready for launch.

7. System ready. Disconnect outside pump motor leads from the internal power supply to stop pumping. Go to the launch site.

B-6.2 At the launch site

1. Connect the sondes with unwinder, parachute and balloon, connect the leads of the pump motor with the power supply. Contact an auxiliary person at the telemetry system that all data are available and reasonable. Launch.

ASOPOS Panel Members

Ozonesonde Meeting of SOP-Experts
30 April – 4 May 2001, Geneva, Switzerland

Hugo DeBacker	Institut Royal Meteo de Belgique, Belgium
Jonathan Davies	Meteo Service of Canada, Canada
Terry Deshler	University of Wyoming, USA
Toshifumi Fujimoto	Japan Meteo Agency, Japan
Bruno Hoegger	MeteoSwiss/PayerneStation, Switzerland
Bryan Johnson	NOAA CMDL, USA
Esko Kyro	Finnish Meteo Institute, Finland
Gilbert Levrat	MeteoSwiss/ Payerne Station, Switzerland
Tom Northam	NASA Wallops Flight Facility, USA
Sam Oltmans	NOAA CMDL, USA
Francoise Posny	University of La Reunion Island, France
Frank Schmidlin	NASA Wallops Flight Facility, USA
Herman Smit	Research Centre Juelich, Germany
Rene Stubi	MeteoSwiss/Payerne Station, Switzerland
Anne Thompson	NASA Goddard Space Flight Center, USA
Pierre Viatte	MeteoSwiss/Payerne Station, Switzerland
Jacquelyn Witte	NASA Goddard Space Flight Center, USA
Michael Proffitt	WMO Environment Division, International

BESOS/ASOPOS-Workshop

"WMO-Workshop for establishment of SOPs for Ozonesondes"
20-23 September 2004, Forschungszentrum Juelich, Germany

Hugo DeBacker	Institut Royal Meteo de Belgique, Belgium
Jonathan Davies	Meteo Service of Canada, Canada
Terry Deshler	University of Wyoming, USA
Toru Sasaki	Japan Meteo Agency, Japan
Bryan Johnson	NOAA CMDL, USA
Dieter Kley	Research Centre Juelich, Germany
Esko Kyro	Finnish Meteo Institute, Finland
Rigel Kivi	Finnish Meteo Institute, Finland
Sam Oltmans	NOAA CMDL, USA
Frank Schmidlin	NASA Wallops Flight Facility, USA
Tom Northam	NASA Wallops Flight Facility, USA
Herman Smit	Research Centre Juelich, Germany
Rene Stubi	MeteoSwiss/ Payerne Station, Switzerland
Anne Thompson	NASA Goddard Space Flight Center, USA
Pierre Viatte	MeteoSwiss/ Payerne Station, Switzerland
Jacquelyn Witte	NASA Goddard Space Flight Center, USA
Michael Proffitt	WMO Environment Division, International, Switzerland

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22. Report of the Fifth Session of the WMO Executive Council Panel of Experts on Environmental Pollution, Garmisch-Partenkirchen, Federal Republic of Germany, 30 April - 4 May 1984 (WMO TD No. 10).

23. Provisional Daily Atmospheric Carbon Dioxide Concentrations as Measured at BAPMoN Sites for the Year 1982. November 1984 (WMO TD No. 12).

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