Quality Control (QC) and Methods

Sample collection and QC

Seawater samples are collected from Niskin-type water bottles at predetermined depths, triggered by a CTD (Conductivity Temperature Depth) unit mounted on a rosette. Two types of CTD have been used on IMR survey ships over the years. The Neil-Brown MK3B and MK3C systems (Commonwealth Scientific and Industrial Research Organisation [CSIRO], Division of Marine Research, Australia) were most commonly used up until the millennium, when it was replaced by Sea-Bird Scientific (SBE) 911plus units (Sea-Bird Scientific, USA). Total number of stations sampled has varied over the years but IMR has, in addition to random visits to the region on short-term projects, made multiple visits to two of the station transects each year (Fugløya-Bjørnøya transect, Vardø-Nord transect). Additionally, an annual, full scale survey covering major parts of the Barents Sea and parts of the Arctic (the Ecosystem cruises) has been done each year since 2003, usually in concert with one or two other ships.

Quality control of large scale, long-term data sets are crucial to account for potential mislabeling, potential errors in storage and handling of the samples leading to contamination, and potential anomalies during analysis of the samples. The *Plankton Chemistry Laboratory* is currently using a QC-flagging system to account for the quality of all the data that are produced. Data with flags 1, 2 and 5 are made available for use in this publication, while flags 3 and 4 are deemed compromised and are not included. Due to the many different people used in the sampling program on IMR cruises, we must accept that minor mistakes can be made. Some of these can be corrected (e.g. a mislabeled depths with a value that clearly belongs somewhere else) and are given Flag = 5, while others are beyond correction (e.g. samples that shows signs of contamination or appears to have been stored too long) and are given flags 3 or 4. An important QC flag is number 2, where we label data points that are outside expected value, but for no apparent reason. Flag number 2 data can be an expression of small term changes that may turn out to be significant over larger time scales, and this kind of data cannot be discarded in ocean monitoring studies lasting decades to centuries. Unfortunately, data from samples collected prior to 2010 discarded flag number 2 labels along with flags 3 and 4. Therefore, flags number 2, 3 and 4 were routinely excluded from data sets during the 1990-2009 period.

Dissolved inorganic nutrients (nitrite, nitrate, phosphate, silicate)

After three rinses, each water sample (20 mL) was collected in a polyethylene vial. Up until the turn of the century (1999-2002) most nutrient samples were analyzed in real time onboard the ships and without chloroform additions. As the research cruise activity expanded, the number of automated analyzers could no longer match the number of ships operating simultaneously and nutrient samples were added chloroform (200 µL) to subdue biological activity and stored at +4 ºC for analysis in the home laboratory within 1-6 weeks. The samples were acclimated to room temperature as the

evaporating chloroform was evacuated by vacuum prior to analysis on an Automated Analysis (AA) system. A number of automated systems have been in use over the years and up until recently, all nutrients were run on homemade Skalar and Alpkem hybrid systems. The latest upgrade was in 2017 when a complete AA system was purchased from Skalar Analytical B.V. (The Netherlands). Colometric determinations of dissolved inorganic nutrients are based on the methods first described by Bendschneider, K. & Robinson, R.I. (1952) and Grasshof (1965) with a number of minor adjustments suggested by the manufacturers (Alpkem, Skalar). The AA system measures nitrate (NO3-), nitrite (NO2-), phosphate (PO4-) and silicate (SiO4-). Briefly, nitrate in seawater is reduced to nitrite coupled to a diazonium ion and, in the presence of aromatic amines, the resulting blue azo-dye is determined spectrophotometrically at 540 nm. The nitrate concentration is corrected for ambient nitrite (same analytical method as for nitrate, but without cadmium reduction) measured concurrently. Ph**osphate** reacts with molybdate at low pH and the resulting phosphomolybdate is reduced with ascorbic acid to a blue complex measured spectrophotometrically at 810 nm. Silicate (silicic acid) is reacting to molybdate at low pH and the resulting silicomolybdate is reduced by ascorbic acid to a blue dye measured spectrophotometrically at 810 nm.

LITERATURE:

Bendschneider, K. & Robinson, R.I. (1952) A new spectrophotometric method for the determination of nitrite in seawater. J. Mar. Res. 2:87-96

Grasshoff, K. (1965) On the Automatic Determination of Phosphate, Silicate and Fluoride in Seawater. ICES Hydrographic Committee Report No. 129

Chlorophyll-*a* and Phaeopigment samples (ChlA, Phaeo)

A standard volume (265 mL) is collected from each depth, collected on a 25 mm GFF filter and stored frozen (-20 ºC) until analysis in the land-based laboratory. Up until recently, pigment samples were transported home by one of the cruise participants, as hand-luggage in a cooler with frozen cooler-elements. These days, pigment samples are brought back in specially designed coolers, with an internal temperature recorder, that is rated for -20 ºC for a minimum of 3 days. In the laboratory, the samples are thawed in 90 % acetone, and stored at +4 ºC overnight before analysis on a Turner Design 10AU fluorometer. Phaeopigments (Phaeo) are measured separately from ChlA, in a second reading of the sample after adding 3 drops of a weak acid (5 % HCl). The fluorometer is standardized regularly using a solid standard with known fluorescence, and in accordance with Holm-Hansen & Riemann (1978) and the manufacturer (Turner Design 1992). Up until 2008 the drift in the light-source was monitored annually, but from 2009 the solid standard has been recorded every time the fluorometer is used.

LITERATURE:

Turner Designs (1992) Model 10-AU-005 Field Fluorometer User's Manual, Version S1C. Turner Designs, California, USA, pp.141

Holm-Hansen, O. & Riemann, B. (1978) Chlorophyll a determination: improvements in methodology. Oikos 30:438-447

Particulate organic carbon and nitrogen (POC, PN) samples

A standard volume (265 mL) is collected from each depth and filtered onto a pre-combusted 25 mm GFF filter (+450 °C, min. 4 h). Each sample is stored frozen (-20 ºC) in a pre-combusted glass tube until analysis in the land-based laboratory. Preparations of samples and analysis of elemental C and N is described in detail in Grasshof et al. (1983). Briefly, the dried filter-samples are fumed in acid (conc. HCl in a desiccator for 4 h), before they are dried again and packed in a tin-foil capsule. Analysis of POC and PN is done on an elemental analyzer and in accordance with the manufacturer's recommendations.

LITERATURE:

Grasshof, K., Ehrhart, M. & Kremling, F. (1983) Methods of seawater analysis (2nd ed). Verlag Chemie, Wiley, Weinheim, pp.410

Dissolved oxygen (oxy) samples

Samples for dissolved oxygen are collected in dedicated glass BOD bottles (approximate volume 125 mL) and filled bottom-up using a Tygon-tubing. The sample is let to overflow approximately 3 times the volume and great care is taken to avoid small air bubbles inside of the sample bottle during filling. Thiosulfate titrations of dissolved oxygen are still done as first described by by Winkler (1888) but the method has seen some updates and improvements in later years (Carpenter 1965, Murray et al. 1968, Strickland & Parsons 1968). Grasshof et al. (1983) describe in detail the current method of sample collection, pretreatment and titrations of Winkler samples. Briefly, dissolved oxygen is reacting with an alkaline solution (Reagent 1) to form a manganese-hydroxy-complex. Under alkaline conditions, the Mn-complex is reacting with the iodide solution (Reagent 2) and left to precipitate in the sample bottle. The sample is added 10 N sulphuric acid to dissolve the iodide precipitate (pH=1-2.5) and the yellow iodine is titrated by thiosulfate to a clear solution. The titrant is standardized by a known concentration of potassium iodate (KIO3) as described by Grasshof et al. (1983).

LITERATURE:

Carpenter, J.H. (1965) The Chesapeake Bay Institute. Technique for the Winkler oxygen method. Limnol. Oceanogr. 10:141-143

Culberson, C.H., Knapp, G., Stalcup, M.C., Williams, R.T. & Zemlyak, F. (1991) A comparison of methods for the determination of dissolved oxygen in sea water. WHP Office Report, WHPO-91-2

Grasshof, K., Ehrhart, M. & Kremling, F. (1983) Methods of seawater analysis (2nded). Verlag Chemie, Wiley, Weinheim, pp.410

Murray, J.N., Riley, J.P. & Wilson, T.R.S (1968) The solubility of oxygen in Winkler reagents used for the determination of dissolved oxygen. Deep-Sea Res. 15:237-238

Strickland, J.D.H & Parsons, T.R. (1968) Determination of dissolved oxygen. In: A Practical Handbook of Seawater Analysis. Fisheries Research Board of Canada, Bulletin 167:71-75

Winkler, L.W. (1888) Die Bestimmung des wasser gelösten Sauerstoffen. Berichte der Deutschen Chemishe Gesellschaft 21:2843-2855