Comparability of Oceanic Nutrient data:

Report from an International Nutrient Workshop Focusing on Phosphate (PO_4) Analysis.

Karel Bakker (1,4); Michio Aoyama (2); E. Malcolm S. Woodward (3); Sharyn Ossebaar (4); Jan van Ooijen (4)

1: SCOR#147 Working Group; NIOZ Royal Netherlands Institute for Sea Research, The Netherlands
2: SCOR#147 Working Group; Fukushima University, Japan
3: SCOR#147 Working Group; Plymouth Marine Laboratory PML, UK
4: NIOZ Royal Netherlands Institute for Sea Research, The Netherlands

Introduction

In order to help improve the world wide comparability of nutrient data a practical analytical workshop at NIOZ (Royal Netherlands Institute for Sea Research), The Netherlands, was held in November 2012 focusing on the analysis of dissolved phosphate (PO_4).

Why?

Although it is agreed that using Certified Reference Material improves the comparability of nutrient data, there are still many issues which arise when using Gas Segmented Continuous Flow Analysers (CFA).

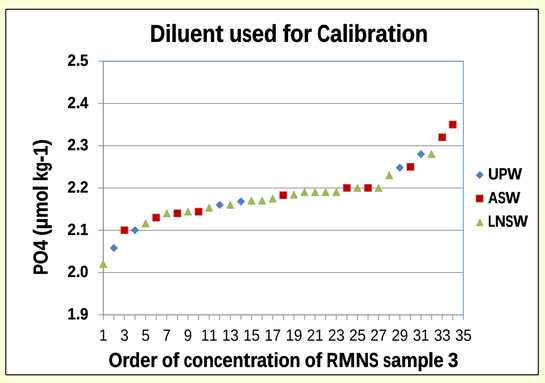


Figure 1.

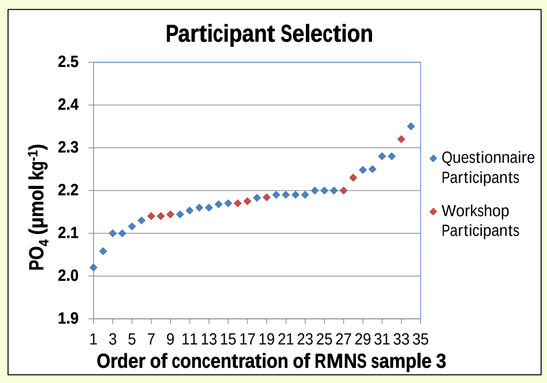


Figure 2.

Figure 1 & Figure 2; PO_4 data for sample 3 of the 2012 Inter Comparison Study of Reference Material for Nutrient Standards (IC RMNS) study showing the large variability of results.

Aim

The aim of the workshop was to gain information about common problems which arise, and then to attempt to investigate these problems in the laboratory, with a small select representative group of international nutrient analysts conducting the lab work. Dissolved PO_4 was focused on as this analyte exhibits most of the common problems encountered when running CFA's.

How?

A questionnaire was sent to all laboratories who participated in the 2012 Inter Comparison Study (IC RMNS) to gain more information about the general problems encountered from the global nutrient analytical community. 18 experts (see figure 2) participated at the workshop and worked simultaneously on four different PO4 gas segmented CFA systems to investigate the identified problems.

Report

The written report documents the findings of the workshop and describes recommendations based on group consensus which can hopefully assist the larger community of labs worldwide participating in the Inter-Calibration Comparison RMNS 2012 studies organized by MRI in Japan.

http://www.scor-int.org/Working_Groups/NIOZReport2012ISBN9784908583018.pdf

Workshop Participants:
C. Anstey[1], M. Aoyama[2], Y. Arii[3], K. Bakker[4], S. Becker[5], S. Coverly[6], A. Daniel[7], P. Hughes[8], M. Kimura[9], A. Murao[9], A. Murata[10], J. van Ooijen[4], S. Ossebaar[4], K. Sato[10], J. Sinke[4], M. Stinchcombe[11], E.M.S. Woodward[12], J.Z. Zhang[13]

Participating Labs:
BIO (Ca) [1], MRI (Jp) [2],Marine Works (Jp) [3], NIOZ (NL) [4], SIO (USA) [5], Seal (Ger) [6] ,IFREMER (Fr) [7], CSIRO (Au) [8], Kanso (Jp) [9] ,JAMSTEC (Jp) [10], NOC (UK) [11], PML (UK) [12] NOAA (USA) [13],

Calculated parameters from information gathered from the participants of the IC RMNS 2012:

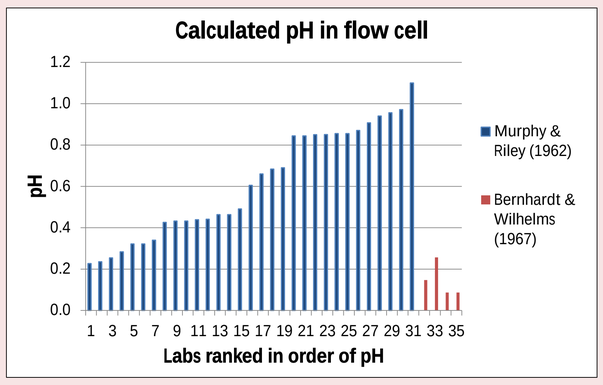


Figure 3.

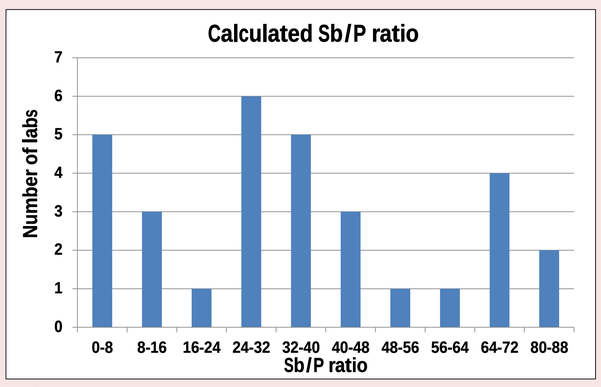


Figure 4.

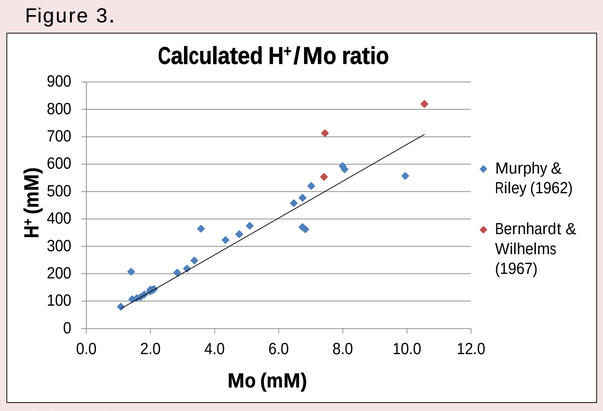


Figure 5.

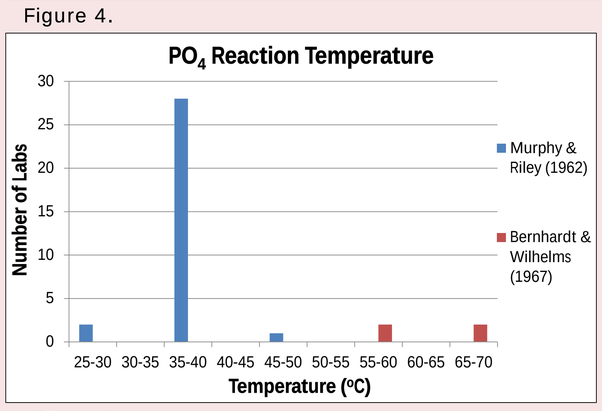
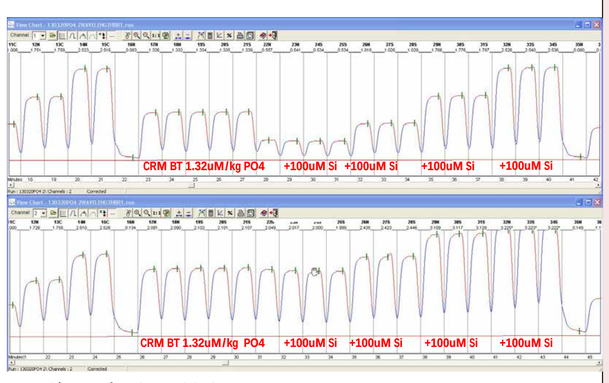


Figure 6.

Some Workshop Results:

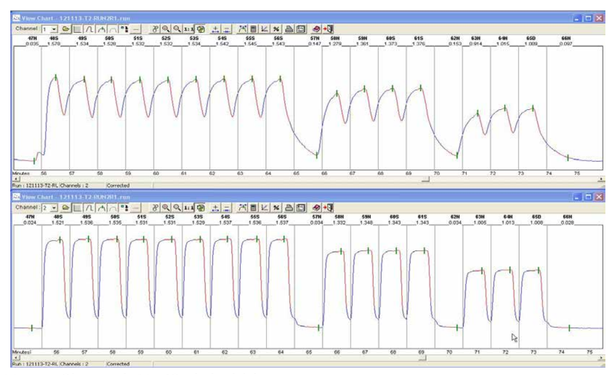
Interference of Silicate detected as PO_4 at two temperatures



Upper Channel: PO_4 at 30ºC.
Lower Channel: PO_4 at 59ºC.

Figure 7.

Inter-Sample (IS) air bubble from pump to manifold



Upper Channel: No IS air bubble.
Lower Channel: with IS air bubble.

Figure 8.

Overview of Report Recommendations

Sb/P Ratio vs Carry-over
The optimal PO_4 colouring with minimum carry-over is at Sb/P ratio 3 to 5.

Choice of Wavelength and Temperature
Consideration of wavelength and temperature depending on the method.
Murphy & Riley (1962) method, wavelength 880nm at 35-40ºC.
Bernhardt & Wilhems (1967) method, wavelength 820nm at 55-58ºC.

Silicate interference
Interference from high silicate concentrations at higher temperatures (59ºC) show that lower reaction temperatures (30ºC) are advisable (see figure 7).

Calibration; standard order vs sample order
It is recommended that the sample concentration order is measured in the same concentration order as the standards due to calibration slope differences.

Sample tray protocol to avoid carry-over
Low concentration samples that are close to the detection limit should be preceded by the baseline.

Sensitivity Drift
It is of major importance to have optimal shaped drift peaks as the computed correction factor will influence the final results. At least duplicate drift peaks should be recorded.

Dispersion factors
The placing and connecting of the correct manifold tubing and glassware is essential. Maintaining the inter-sample bubble through the peristaltic pump tubing is essential to minimise the effect of dispersion (see figure 8).

NIOZ is an institute of NWO in cooperation with Utrecht University