INTRODUCTION

Nutrient enrichment of coastal waters is a world-wide problem. Human activities have resulted in an increase of nutrients, especially nitrogen and phosphorus, to the marine environment. Nutrients can enter the marine environment from domestic wastes, agricultural run off, animal wastes and atmospheric discharges. In coastal areas, this enrichment of nutrients can result in eutrophication, which in turn leads to low dissolved oxygen and poor water quality. Concerns have also been raised over the effect on the open ocean. There is therefore a requirement to investigate their effect on the delicate balance of the marine ecosystem.

Inorganic nutrients provide an essential function in the food web structure of the marine ecosystem. Micronutrients, such as nitrogen, phosphorus and silicon, in their inorganic forms, promote the healthy growth of phytoplankton. The phytoplankton is utilised by zooplankton, which in turn supports stocks of pelagic fish.

To improve the sensitivity and precision of inorganic nutrient analysis in seawater, the outdated Autoanalyser at FRS was replaced by a state of the art Bran+luebbe Autoanalyser 3 (AA3). Evaluation of the new AA3 was performed both in the laboratory and at sea, on board the FRV Scotia IV during a hydrographic monitoring cruise of Scottish and oceanic waters.

METHODS

Total oxidised nitrogen (ToxN)

Old Autoanalyser

- Method based on that developed by Wood et al.¹ and Beneschnicder & Robinson²

AA3

- Method based on the nitrate determination in standard methods and in the DIN/ISO standards for automatic nitrate measurements.

Phosphate

Old Autoanalyser and AA3

- Methods based on that developed by Murphy & Riley³

Silicate

Old Autoanalyser and AA3

- Methods based on that of Korent⁴

Water collection and analysis at sea

Water samples were collected at sea from the FRV Scotia IV by means of a Rosette Sampler (Figure 1). Collected water samples were stored in ice until analysis could be undertaken, no longer than 6 hours after collection.

Figure 1. Deployment of Rosette sampler from FRV Scotia IV

EVALUATION OF NUTRIENT ANALYSIS WITHIN THE LABORATORY

The method was validated, in the laboratory, by determining the precision, accuracy and limit of detection (LOD) of each nutrient method. The LOD of the AA3 instrument for ToxN and silicate was ten times lower than that of the old instrument, with precision also being improved for all parameters except phosphate at the high standard.

EVALUATION OF THE BRAN AND LUEBBE AA3 AT SEA

Problems with AA3 at sea

- Contamination of sample.
- The signal for the silicate and phosphate was found to be extremely unstable while the ship was moving.
- In extremely rough weather the noise on the phosphate channel was as much as 30%. However the baselines returned to normal when the ship docked.

Causes

- Background contamination in containerised laboratory.
- Vibration of sample inside the lamp source.

Solutions

- Design and fitting of auto-sampler cover, to reduce background contamination.
- Software smoothing of the AA3 was applied to the baselines, but even at its highest function the noise was not reduced sufficiently to allow analysis.
- AACE software was modified to take the sample and reference beams simultaneously.
- Stabilisation of the CE2000 at sea for an extended period.
- The tungsten filament was replaced with a light emitting diode (LED), Significant improvements were observed (Figure 2).

Validation of AA3

Following the replacement of the tungsten filaments with LED photometers, to each of the channels, the instrument was validated at sea and revalidated in the laboratory.

Phosphate

An additional high silica standard (high st22) was used as very high concentrations of silicate can be found in the deeper waters.

Sides-standard deviation

The laboratory stock solution was from a freshly opened which had a different concentration from that used at sea, resulting in differences in results.

CONCLUSIONS

- The AA3 is superior to the old instrument, having lower LOD, increased sample throughput and reduced matrix effects.
- Extensive work at sea with the instrument designer has resulted in the production of a new detector with an LED as the light source for each parameter.
- The new detector combined with the modified software has eliminated baseline noise at sea.
- The Bran & Luebbe AA3 has been fully validated and accredited by UKAS for the analysis of nutrients in seawater both in the laboratory and at sea.

REFERENCES

2. Gerlach, S.A., Nutrients as a Cause, Environmental protection of the North Sea, 1968, pp. 10-175