

HIGH PRECISION CHROMATOGRAPHY ANALYSIS OF NITROUS OXIDE AND METHANE IN SEAWATER.

REPORT ON THE SHORT TERM SCIENTIFIC MISSION (STSM)

COST-STSM-735-4997

BENEFICIARY'S NAME AND INSTITUTION:

Mercedes de la Paz Arándiga,
Marine Research Institute-CSIC, Vigo, Spain.

HOST'S NAME AND INSTITUTION:

Prof. Robert Upstill Goddard.
School of Marine Science and Technology, University of Newcastle upon Tyne, United Kingdom

PERIOD:

1/10/2009 to 15/12/2009

MOTIVATION:

My research is focused on air-water CO₂ exchange and associated biogeochemical processes, mainly in coastal waters. This activity is lead by Fiz Perez and Aida Rios. We are highly motivated towards incorporating measurements of N₂O and CH₄ in coastal ecosystems into our work. This will allow us to more completely assess the magnitude of greenhouse gas emissions from the coastal ocean. The purpose of this STSM was to visit the laboratory of Professor R. Upstill-Goddard (Ocean Research Group; Newcastle University), in order to receive training in the simultaneous, high precision measurement of N₂O and CH₄ in seawater and in atmospheric air by single-phase equilibration gas chromatography (SPE-GC) using flame ionization (FID: CH₄) and electron capture (ECD: N₂O) detection.

SUMMARY OF ACTMTIES:

In order to become familiarised with the theory and practice of the SPE-GC technique, several tasks were performed under the guidance of Dr. Jonathan Barnes and the supervision of Prof. Robert Upstill-Goddard. The analytical apparatus used was a modified version of one described in detail by Upstill-Goddard et al., (1996).

The coupled equilibration-GC system was first run manually without the use of the software that fully controls all GC chromatography valves switching and ancillary operations. This task enabled me to identify and gain insight into the operation of, each of the principal components of the SPE:GC. It was especially useful to match the switching of the different chromatography valves with the different paths through which these direct water samples, atmospheric air or calibration standards.

The resolution of some unexpected problems with the automated control of the SPE-GC gave me a valuable opportunity to gain a deep understanding of the automation of the SPE:GC. I

was able to identify the components, functions and troubleshooting aspects of the data processing units and also the sequence of events that run the analytical system automatically.

Once all the automation problems of the GC were solved, different analytical routines were developed, i.e. :

- Stabilisation of the base line of the ECD and FID detector: identification of the main sources of the base line noise, especially for the N₂O analysis.
- Maintenance and troubleshooting for a clear and reproducible signal in the chromatogram.
- Manual integration of sample peaks as required.
- Calibration
- Standardisation of the compressed air used during the water sample equilibration process.

Some local water and atmospheric air samples were collected from the Tyne estuary, at Newburn Bridge, which is located 23 km upstream of the estuary mouth. During sample collection special attention was paid to identifying the major issues that should be addressed during the sampling and storage procedures. On return to the Newcastle laboratory water samples to be analysed were first warmed at 25 °C in a thermostatic water bath. All samples were analysed within a few hours of collection. Following sample analysis the raw sample peak areas were converted to in situ N₂O and CH₄ water partial pressures and concentrations using standard solubility equations and by applying a phase-partitioning correction based on water sample and headspace volumes during the equilibration step, and the N₂O and CH₄ mixing ratios in the equilibrator gas (compressed air)..

All these activities have the purpose of allowing the development of sufficient competence for the unsupervised operation of the GC.

The second general objective of the STMS was to transfer the SPE-GC technology to the Marine Research Institute-CSIC in Vigo in order to develop a high precision N₂O and CH₄ analytical capability there. A detailed list of the full specifications of the SPE:GC system component parts and the relevant suppliers was assembled during my stay in Newcastle. Furthermore, I engaged in fruitful discussion with Dr. Barnes regarding possible improvements that could be incorporated in the design and construction of a new SPE:GC with the technology currently available.

OUTCOMES:

This STSM allowed me to develop a detailed knowledge of the methodology behind the measurement of N₂O and CH₄ in seawater and atmosphere air using gas chromatography. The training covered all aspects of the method and troubleshooting, and the components and parameters to be controlled for accurate measurements of these trace gases in seawater.

This expertise will be transferred during January 2010 when I will begin constructing a new SPE:GC system for measuring of N₂O and CH₄ in the Oceanography Department of the Marine Research Institute (CSIC) in Vigo. This will involve further collaboration with Prof. Robert Upstill-Goddard.