CHEMINI: CHEMICAL MINIATURISED ANALYSER

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1. Introduction
The development of in situ analysers to make chemical measurements in marine environment seems nowadays essential to allow the chemical characterisation of habitats prevailing in hydrothermal vent ecosystems. In situ chemical analysis offers numerous advantages such as the limitation of the modification of the sample with an immediate analysis, the possibility to perform high frequency automated measurement giving an access to steep chemical gradients, the potential to do real-time survey and in situ calibration. In situ chemical analysis is made possible by the use of flow analysis. Several types of field analysers have already been developed in Ifremer during the 90's. It is the case of the deep sea version « Alchimist » [1] (certified for depths down to 6000 m), used for the determination of iron and sulphur in hydrothermal zones and also for the determination of subnanomolar concentrations of iron in coastal waters[2].

"CHEMINI" constitutes the new generation of analysers developed by Ifremer within the department Technology of the Instrumental Systems for the measurement of sea water chemical parameters. The choice of elements composing this new generation was made according to several rules: reliability, analytical performances, miniaturization to easily implement CHEMINI on deep submersibles, consumption (energy and reagent), and costs.

2. Results and discussion
CHEMINI (cf. Fig.1) is a mono parameter in situ chemical analyser and is assimilated to a sensing element. Several advantages are arising from this concept, the ability to make simultaneous measurements, the independence of each measurement, a reliability increase, the possible use of different detection methods, the modularity of the system (1, 2, 3 or more parameters). The analysers can be set serially on a sampling line and controlled by a single software. CHEMINI can be integrated on different vectors (ROV, AUV, seabed station…) and be used in a teleoperated mode or in an autonomous way. The deep-sea version of CHEMINI allowing the in situ determination of iron[3] and sulphide[4] was developed during the EXOCET/D European project.

Figure 1 CHEMINI deep sea version 2.1 Concept

CHEMINI is built around two modules:
The hydraulic module is an equipressurized tank filled with dielectric oil (right handside in Fig.1). Two peristaltic pumps and eight 3-port SMC solenoid valves are used for circulation of the different fluids: reagents, standards and samples. Three solenoid valves constitute the injection system whereas 5 ones build a 6 ways selection system. Most of the manifold tubing is replaced by an engraved circuit in PMMA. The pumps and valves are integrated directly on the manifold limiting the use of tubing and connecting parts. The detection module (left handside in Fig.1) holds the electronic cards and the colorimeter in a pressure tank in Titanium. The quartz flow cell, manufactured by HELLMA, is placed outside this tank. The light is emitted by LEDs to the external quartz flow cell and returns to the colorimeter board via optic fibres and special waterproof titanium optic pass through (SEDI). Much of the development effort on this in situ analyser has focused on miniaturisation. Its low weight (12,6 kg without reagents) and small dimensions (130mm H x 148mm L x 120mm l for the hydraulic module and 264mm H x 140mm D for the detection module) permits simple and accommodating operations for on site deployment, speaking of implementation on submersible, long-term benthic station and at sea maintenance. 2.2 Chemical specifications and performances

The chemical parameters to be measured are total sulphide (ΣS) and total iron (FeII + FeIII). The analytical methods based on colorimetric detection have been extensively studied at Ifremer [1, 3, 4]. Other parameters are envisaged and the analysers will be versatile for existing chemical analysis methods (nitrite, nitrate, phosphate, silicate, pH, pCO2…) and opened for new developments. CHEMINI is the new generation of chemical analyser and is able to work with the various principles of flow analysis (FIA, CFA, stop flow, …).2.3 At sea trials
During the MOMARETO cruise[5] (Azores, MoMAR zone, august 2006), trials were performed in two steps corresponding to the two legs of the cruise. The first leg was partly focussed on the technical validation of CHEMINI. The second leg was devoted to the operational use of CHEMINI to characterize the spatial distribution of mussel's assemblages on the Eiffel Tower hydrothermal edifice. CHEMINI was used on a remote controlled mode implemented on the ROV VICTOR. The sample lines of the two CHEMINI were directly connected to the ROV sample inlet with 2 ways available for each CHEMINI in case of plugging. The two CHEMINI have been involved in twelve dives, doing 631 samples measurements for total iron and 524 samples measurements for total sulphide with periodic in situ calibration. During the last days of the cruise, CHEMINI Iron has been implemented on the TEMPO autonomous seabed station coupled to the AIM video camera and an autonomous temperature sensor. The whole system has been deployed on the Lucky Strike site for one year. The sample inlet was positioned by Victor in a mussel bed. The measurement rate was set at 8 measurements per day. The recovery is planned in July 2007.

3. Conclusion
Two prototypes of CHEMINI deep-sea are available and operational to perform total sulphide and total iron measurements in hydrothermal environments. We have succeeded in decreasing the dimensions of the analyser with a real miniaturised system easy to implement in different vectors such as the ROV Victor or the TEMPO monitoring station. CHEMINI integrates some innovative parts like the engraved manifold and the detection module. This module allows obtaining in situ analytical performances similar to laboratory products. Last, the system has proved a very good reliability during the final demonstration cruise with a number of dives and data obtained never reached before. The two analysers have been validated during the first leg of

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5. References

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SMOS: MEASURING SEA SURFACE SALINITY FROM SPACE

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1. Introduction

The distribution and variability of salinity in the world's oceans is a key parameter to understand the role of the oceans in the climate system. However, until now, remote sensing of the sea surface salinity (SSS) from space has not been attempted.

SMOS (Soil Moisture and Ocean Salinity) [1], due to be launch by end 2008, is a European Space Agency mission that aims at generating global ocean salinity maps with an accuracy of 0.1 psu, at spatial and temporal resolution suitable for climatic studies. The satellite sensor is an L-band (1400–1427 MHz) aperture synthesis interferometric radiometer [2]. Sea surface salinity (SSS) can be retrieved since the brightness temperature of sea water is dependent on the frequency, angle of observation, dielectric constant of sea water, sea surface temperature and sea surface state.

The SSS maps are expected to have an accuracy of 0.1 psu at a spatial resolution of 100–200 Km every 10–30 days. The individual measurement is expected to have an accuracy of 1psu with a resolution of 15 Km.

Salinity modifies the dielectric constant of sea water and it is one of the parameters that determine the sea surface emissivity [3]. At L-band, a restricted band for passive observations, the brightness temperature (Tb, measure of the sea surface emission) presents a maximum sensitivity to SSS. However, the sensitivity is quite low: 0.5 K/psu at sea surface temperature (SST)=20 ºC, and decreases to 0.25 K/psu at SST=0 ºC [4]. Moreover, Tb at this frequency is also sensible to sea surface roughness, 0–0.4 K/(m/s), (when roughness is parameterised in terms of wind speed) depending on the incidence angle [5], and to SST, 0.2–0.4 K/ºC. This situation indicates that it is necessary to have an accurate knowledge of the surface roughness and SST (auxiliary parameters) to retrieve salinity with enough accuracy.

To increase the present understanding of the sensitivity of Tb to wind speed and direction at L-band, the European Space Agency (ESA) sponsored the WInd and Salinity Experiments (WISE). These experiments aimed, among other activities, at improving and validating the actual sea surface emissivity models at L-band [6].

2. Campaigns and ongoing studies

WISE 2000 and 2001 took place at the Casablanca oil rig platform in the Mediterranean Catalan coast, at 40º 43.02' N 1º 21.50' E, 40 Km offshore [7]. They were performed during one month in autumn, when maximum wind speed is expected in the region. An L-band full-polarimetric radiometer measured Tb from 33 m above sea level at differ-