



Simultaneous determination of CFC-11, CFC-12 and CFC-113 in seawater samples using a purge and trap gas-chromatographic system

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ABSTRACT

We have optimized the analytical parameters of a homemade instrument for the simultaneous measurement of the chlorofluorocarbons CCl_2F_2 (CFC-12), CCl_3F (CFC-11) and $\text{C}_2\text{Cl}_3\text{F}_3$ (CFC-113) in seawater. Seawater samples are flame sealed into 60 ml glass ampoules avoiding any contact with the atmosphere and stored in cold, dark condition until analysis. In the laboratory, after cracking the ampoule in an enclosed chamber filled with ultra-pure nitrogen, the seawater sample is transferred to a stripping chamber, where ultra-pure nitrogen is used to purge the dissolved CFCs from the seawater. The extracted gases are then cryogenically trapped, subsequently the trap is isolated and heated and the CFCs are transferred by a carrier gas stream into a precolumn and then are separated on a gaschromatographic packed column. To separate adequately CFC-12 from N_2O , during the early part of the chromatographic run, the gas stream passes through a molecular sieve, which is then isolated and backflushed. The CFCs are detected on an electron capture detector (^{63}Ni ECD). After a careful choice of the experimental conditions, the performances of the system were evaluated. The detection limits for seawater samples are: $0.0081 \text{ pmol kg}^{-1}$ for CFC-12, $0.0073 \text{ pmol kg}^{-1}$ for CFC-11 and $0.0043 \text{ pmol kg}^{-1}$ for CFC-113. The reproducibility of replicate samples lies within 5% for the three CFCs. The system has been successfully employed for CFC measurements in seawater samples collected in the Ross Sea (Antarctica) in the framework of the Italian Antarctic research project.

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1. Introduction

Several chemical compounds have been widely used as tracers of ocean circulation and mixing processes. They include nutrients and dissolved oxygen, which have a natural background level and a quasi-steady state distribution in the deep ocean, radiocarbon and tritium, which have background levels significantly altered by human activities and anthropic compounds such as chlorofluorocarbons (CFCs).

Production and release of CCl_2F_2 (CFC-12) and CCl_3F (CFC-11) in the atmosphere began in the 1930s and increased rapidly during the following five decades. Differently, the atmospheric concentration of $\text{C}_2\text{Cl}_3\text{F}_3$ (CFC-113) increased rapidly during the 1980s. CFCs are volatile, chemically stable and characterized by rapid mixing rates within the lower atmosphere, so their tropospheric concentrations are relatively uniform. The CFC concentrations in the atmosphere can be reconstructed as functions of location and time [1]. Atmo-

spheric CFCs cross the air-sea interface and dissolve in surface seawater; their equilibrium concentrations can be calculated as a function of seawater temperature and salinity and atmospheric gas concentration [2]. Indeed, CFCs have a time-dependent oceanic input. Although the degradation of CFCs in marine environment under reducing conditions (such as fjords) was reported [3], in well-oxygenated waters (such as oceanic waters) they are chemically stable. Thus, they can serve as transient tracers of the ocean circulation.

Oceanic CFC measurements have been widely used to evaluate the variability of water mass formation and rates of ocean ventilation [4–7], to assess ocean circulation and climate models [8–13] and to quantify the ocean uptake of anthropogenic CO_2 [14–17]. CFCs are often used to calculate the “age” of a water sample, commonly defined as the time elapsed since the water parcels contained in the water sample lost direct contact with the atmosphere [18].

Volatile and semi-volatile organic compounds account for a large part of chemicals of environmental interest, which are analyzed by gas chromatographic (GC) methods. Several compounds, including CFCs, have low concentration levels in aqueous samples and the most used GC detectors are not able to detect them. For this reason, the sample preparation becomes essential. Further,

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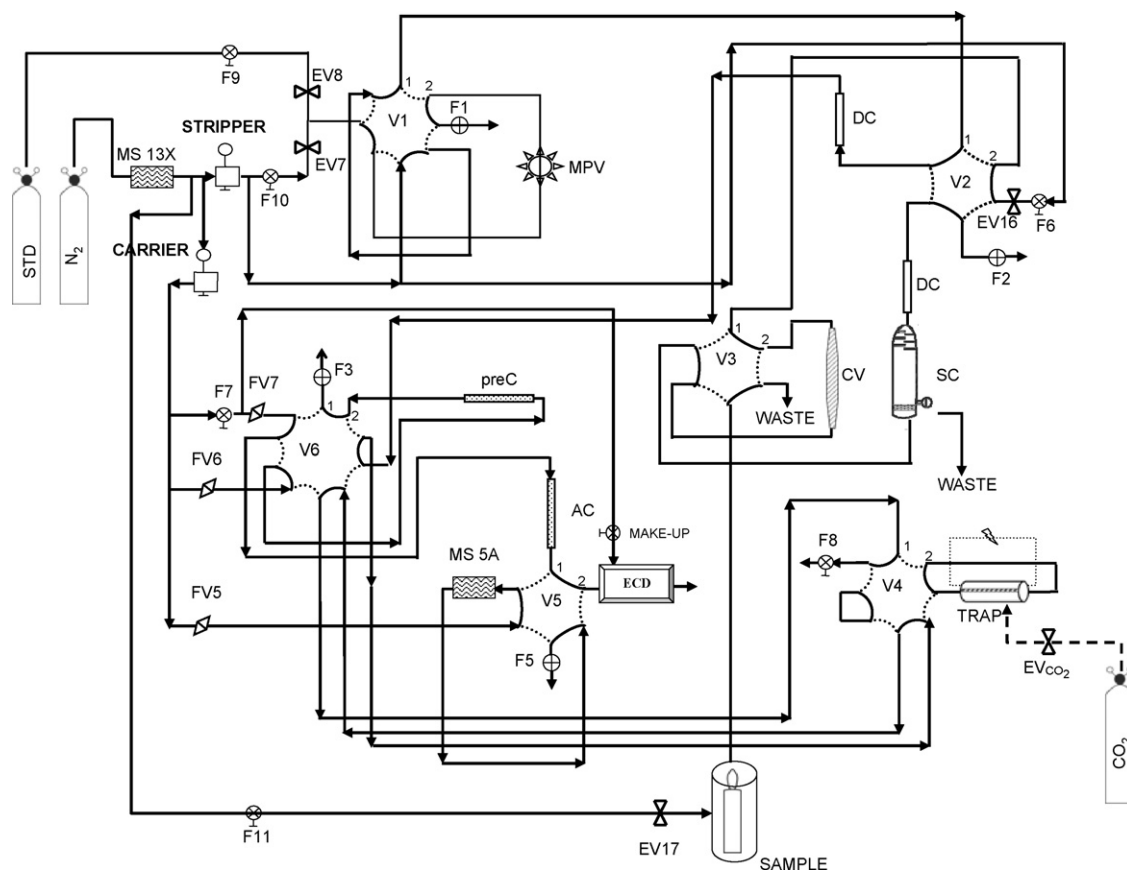


Fig. 1. Schematic flow scheme of the CFC extraction and analytical system in “stand by” mode. Tubing connecting all the components are stainless steel (SS). All the valves are electrically actuated under program control. For abbreviations see Table 1.

the number of operations and processes involved in the sample preparation stage should be kept to a minimum.

The CFC-11 and CFC-12 analysis in seawater was introduced by Bullister and Weiss [19] and it has been widely used in the succeeding years. The introduction of the CFC-113 measure, the necessity to improve the data quality and to reduce the sample contamination, the aim to shorten the analysis time and to eliminate most of the manual procedures encourage several laboratories to develop ocean tracer methods and measurements [8,20–22].

This paper describes the optimization of the main instrumental parameters of a purge and trap-gas chromatographic system for the simultaneous determination of CFC-11, CFC-12 and CFC-113 in seawater samples. Particularly, a thorough study of the CFC stripping from the seawater samples was carried out. The purge and trap system was built in our laboratories following the design provided by W. Smethie and E. Gorman (LDEO, Columbia University, New York, USA). Some design modifications have been made. They mainly concerned the ampoule housing, the nitrogen flow regulation and the trap heating system. These modifications are described in Sections 2.1 and 2.4. The optimized analytical system has been used to analyze seawater samples collected in the Ross Sea (Antarctica) during the austral summer 2002–03 Italian Antarctic Expedition.

2. Experimental

2.1. Apparatus

The apparatus consists of a purge-and-trap system interfaced to a gas chromatographer (GC) equipped with an electron capture detector (ECD). The purge and trap system and the interfacing devices were built in our laboratories following, and partially mod-

ifying, the instrumental schemes provided by W. Smethie and E. Gorman (LDEO, Columbia University, New York, USA). A part of the apparatus is devoted to gas analysis and it is used for calibration with standard gas mixture, while another part is devoted to CFC extraction from water samples.

The flow scheme is shown in Fig. 1, while Table 1 lists the main components of the analytical system.

Ultra-high purity nitrogen (N_2) is used as both stripping and carrier gas. Pressure from the gas cylinder is reduced to approximately 7 bar using a high purity pressure regulator. To remove CFC impurities present in the nitrogen supply, N_2 flows through a trap (molecular sieve MS 13X 60/80 mesh) held at room temperature. The trap is reconditioned by heating to 200 °C and by purging with a reverse N_2 flow of several hundred $ml\ min^{-1}$ for about 4 h. The MS 13X reconditioning is required when the baseline increases during the analysis of system blanks due to a gradual CFC release from the trap. The nitrogen, downstream from MS 13X, is divided into three pathways: carrier gas, stripper gas and make up gas straight directed to the ECD. The upstream pressure of the stripper gas and of the carrier gas is adjusted to 2.0 bar and to 3.0 bar respectively, using two pressure regulators. We modified the Smethie's design by adding a needle valve for the fine adjustment of the carrier gas flow rate (approximately $30\ ml\ min^{-1}$ as measured at the ECD inlet) (cf. F7 in Fig. 1). In addition, we split the carrier gas stream into three ways, each of them provided with an on/off valve (cf. FV5, FV6, FV7 in Fig. 1). This adjustment helped us in the leak procedure test and allowed a separate cleaning of the analytical column and the molecular sieve 5 Å, improving the control of the system contamination. The standard gas inlet is connected to a cylinder of a compressed calibration standard gas mixture, which is injected into the analytical system through an electro-valve (EV8). The sam-

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