CHINESE JOURNAL OF ANALYTICAL CHEMISTRY
Volume 44, Issue 7, July 2016
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Chin J Anal Chem, 2016, 44(7), 1003–1008.

RESEARCH PAPER

Simultaneous Determination of Chlorofluorocarbons and Sulfur Hexafluoride in Seawater Based on a Purge and Trap Gas Chromatographic System

CAI Ming-Gang[1,2,*], DENG Heng-Xiang[1], HUANG Peng[1], KE Hong-Wei[1], ZHENG Xue-Hong[1], LI Wen-Quan[1]

[1] College of Ocean and Earth Sciences, Xiamen University, Xiamen 361102, China
[2] State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361102, China

Abstract: Chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6) are types of anthropogenic halogenated compounds, and are very important for ocean processes, including air-sea and water mass exchanges. Meanwhile, they can also be used to calculate some key physical and biogeochemical parameters such as the apparent oxygen utilization rate and anthropogenic CO_2. Compared to CFCs, SF_6 is quite difficult to measure in seawater due to its low solubility. However, it is useful to study the ocean processes based on both CFCs and SF_6. In this study, a purge and trap gas chromatography system was developed to simultaneously measure CFC-12 and SF_6 in seawater. The optimal conditions were as follows: trap temperature of –70 °C, purge time of 8 min, purge gas pressure of 310 kPa, desorption time of 30 s, desorption temperature of 90 °C. The method was simple and sensitive. The detection limit were 0.02 pmol kg^{-1} for CFC-12 and 0.03 fmol kg^{-1} for SF_6. The analytical precision of CFC-12 was ±1.2% and that of SF_6 was ±0.5%. The correlation coefficient (R^2) values of all calibration curves were greater than 0.9995. This method was successfully used in the analysis of sea water samples collected during the 6th Chinese Arctic Research Expedition.

Key Words: Sulfur hexafluoride; Chlorofluorocarbons; Purge and trap; Gas chromatography; Seawater

1 Introduction

Chlorofluorocarbons (CFCs) are a group of synthetic halogenated methanes, natural sources of which are usually insignificant[1]. Sulfur hexafluoride (SF_6) is also a synthetic compound which has been used in the electrical industry since the 1960s. It is an inert, nontoxic, non-corrosive gas, which makes it widely applicable to metal smelting.

Entry of CFCs and SF_6 into the ocean is through air-sea exchange. They are extremely stable gases in the ocean with unique physical and chemical properties. One of the main advantages is that the time-dependent source function permits calculation of rates for ocean processes. Therefore, CFCs and SF_6 were widely used as tracers of ocean circulation and mixing processes[2]. Their timescale information could be used to estimate rates for physical and important biogeochemical processes, such as the calculation of the apparent oxygen utilization rates[3–7], and anthropogenic CO_2 inventories[8–12].

CFC concentrations are at most 10^{-12} M, and SF_6 concentrations at 10^{-15} M in seawater. Because of their extremely low concentration level and the possibility of contamination by compounds in the atmosphere[13], the measurement of CFCs, and especially SF_6, in the ocean is difficult. With the development of analytical techniques, a

Received 2 February 2016; accepted 25 March 2016
*Corresponding author. Email: mgcai@xmu.edu.cn
This work was supported by the National Natural Science Foundation of China (Nos. 40976113, 41076113, 91228202), and the Polar Environment Investigation and Assessment Supported by the Chinese Arctic and Antarctic Administration (CHINARE2014-03-04-03), the Fund of Key Laboratory of Global Change and Marine-Atmospheric Chemistry, SOA, (GCMAC1404), the Program for New Century Excellent Talents in Fujian Province University, and the Fundamental Research Funds for the Central Universities of China.

DOI: 10.1016/S1872-2040(16)60941-6

method for the simultaneous measurement of SF_6 and CFCs in seawater samples with an improved analytical system was reported[14]. Based on this, a method for rapid, automated shipboard analysis of dissolved SF_6 and CFC-11, CFC-12 in small volume seawater samples was developed by Bullister *et al*[15]. So far, the reliability of CFC measurements is similar to the routine measurement of dissolved oxygen and nutrients[13], but for SF_6 measurement, there is still a great potential for improvement because of their low concentration and solubility in seawater.

In China, the researches on methods for determination of SF_6 and CFCs are still in their preliminary stage, mainly focusing on CFC measurement[16–18]. After continuous improvement, an analytical technique for simultaneous measurement of multiple CFCs was developed, with significantly improved sensitivity[18]. However, the research in China on the measurement of SF_6 in seawater is still a gap. Therefore, it is necessary to carry out further research on simultaneous measurement of CFCs and SF_6.

Because of the extremely similar distribution of CFC-11 and CFC-12[19,20], only the concentration of CFC-12 and SF_6 were measured simultaneously in this study. The measurements were made using a purge and trap technique and gas chromatography with electron capture detector (ECD). Standard gas and a packed column were used for calibration and separation. The operating conditions, in particular trap materials, trap temperature, switching time, purge time, and purge efficiency, were evaluated and optimized. The analytical precision and limit of detection were also evaluated. The system was successfully used in the analyses of samples collected during the 6th Chinese Arctic Research Expedition. The stability, precision and the results reached the same level as those of the same kind of instrument elsewhere.

2 Experimental

2.1 Instruments and chemicals

Gas chromatography with ECD (Techcomp (Holdings) Limited, China; original Varian, USA), a purge and trap system (built by ourselves), a packed main column (180 cm Carbograph1 AC + 20 cm Molsieve 5A, 3.175 mm OD), a packed pre-column (30 cm Porasil C + 60 cm Molsieve5A, 3.175 mm OD), a trap (1.6 mm OD, packed with 50 cm Porapak T, grain size of 0.18–0.25 mm), and a gas flowmeter were used.

Dry ice, ultra high purity nitrogen (99.9995%), absolute ethanol (AR grade) were used. CFCs and SF_6 standard gas (2.62 μg m^{-3} for CFC-12, 0.048 μg m^{-3} for SF_6) were from National Oceanic and Atmospheric Administration, USA. Six-port, four-port, three-port and multiport valves were bought from VICI company USA. Regulator was purchased from Parker Hannifin, USA and loops (0.1, 0.25, 0.5, 1.0, 2.0 and 5.0 mL) were purchased from VICI company, USA.

2.2 Experimental method

The purge and trap technique is a currently commonly used techniques for the enrichment of volatile substances in water[21,22], with low injection volume and high detection sensitivity. The six-port valve and various loops, which were used for standard gas injection, were added to the purge and trap system built by ourselves. The schematic illustration of the system is shown in Fig.1. V1 was a multi-position valve to select gas sample streams (standard, blank, air). V2 and V3 were six-port valves with calibrated sample loop. V4 was a six-port valve for connecting or isolating the purge chamber from the rest of the system. V5 was a four-port valve, manually operated, used to vent the head space of the purge chamber while it was being filled with a water sample. V6 was a six-port valve for isolating the trap at standby or while the trap was heating. V7 was a six-port valve, for switching the

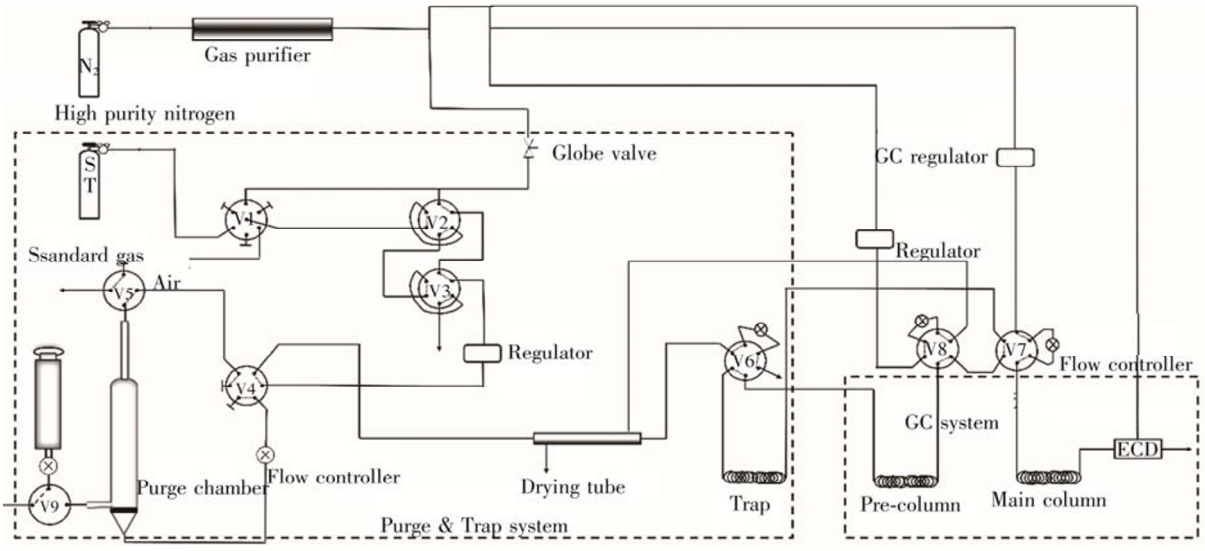

Fig.1 Diagram of purge and trap system for CFC-12 and SF_6 measurements