

学校编码: 10384

密级\_\_\_\_\_

学号: 22320131151379

厦 门 大 学

硕 士 学 位 论 文

**楚科奇海和大亚湾胶体有机物的组成和粒  
径分布—非对称流场场流仪的应用**

**Composition and size distribution of colloidal organic  
matter in the Chukchi Sea and Daya Bay: Application of  
asymmetric flow field-flow fractionation**

林 辉

指导教师姓名: 陈 敏 教 授

专 业 名 称: 海 洋 化 学

论文提交日期: 2016 年 5 月

论文答辩时间: 2016 年 6 月 s

2016年5月

## 厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下，独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果，均在文中以适当方式明确标明，并符合法律规范和《厦门大学研究生学术活动规范（试行）》。

另外，该学位论文为（海洋与地球学院同位素海洋化学）课题（组）的研究成果，获得（海洋与地球学院同位素海洋化学）课题（组）经费或实验室的资助，在（海洋与地球学院同位素海洋化学）实验室完成。（请在以上括号内填写课题或课题组负责人或实验室名称，未有此项声明内容的，可以不作特别声明。）

声明人（签名）：

年 月 日

## 厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

1. 经厦门大学保密委员会审查核定的保密学位论文，  
于 年 月 日解密，解密后适用上述授权。

2. 不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年 月 日

# 目录

摘要.....	V
Abstract.....	XI
缩略词.....	XIII
第 1 章 绪论.....	1
1.1 海水中胶体有机物的地球化学行为.....	1
1.2 海水中胶体有机物的浓缩分离技术.....	4
1.2.1 超滤技术.....	4
1.2.2 固相萃取技术.....	7
1.2.3 反渗透-电渗析技术.....	8
1.3 海水中胶体有机物的检测技术.....	10
1.3.1 光谱技术.....	10
1.3.2 核磁共振谱和傅里叶变换-离子回旋-质谱技术.....	14
1.4 场流分离技术及其在海洋科学中的应用.....	14
1.5 本研究的目的是和内容.....	16
第 2 章 研究方法.....	17
2.1 搅拌池超滤预富集.....	17
2.2 搅拌池超滤的截留效率.....	18
2.3 非对称流动场场流仪简介.....	19
2.4 非对称流动场场流仪的粒径分离原理.....	24
2.4.1 层流.....	24
2.4.2 爱因斯坦-斯托克斯关系(动力学原理).....	24
2.4.3 AF4 管道剖面的层流速率.....	25
2.4.4 分子扩散模型.....	27
2.5 定量环和增压管的改装.....	29

2.6 样品预处理方法的确定.....	31
2.7 AF4 系统参数的选择.....	33
2.7.1 载液的选择.....	33
2.7.2 粒径刻度中标准物质的选择.....	34
2.8 检测器线性响应状况及样品的重复性检验.....	37
2.8.1 紫外-可见吸光检测器的平行性检验.....	37
2.8.2 样品测量的重复性检验.....	37
2.8.3 检出限的确定.....	39
2.8.4 粒径谱曲线的积分方法.....	40
2.9 AF4 测量胶体有机物粒径大小的方法.....	42
2.10 其他相关参数的测量.....	44
2.10.1 吸光光谱.....	44
2.10.2 三维荧光光谱测量.....	45
2.10.3 DOC 浓度测量.....	45
2.11 结论.....	46
<b>第 3 章 楚科奇海胶体有机物的组成和粒径分布.....</b>	<b>47</b>
3.1 引言.....	47
3.2 样品采集与分析.....	49
3.2.1 样品采集.....	49
3.2.2 样品预处理.....	49
3.2.3 分析方法.....	51
3.3 结果.....	52
3.3.1 楚科奇海 R 断面的水文、DOC 和 CDOM 光学性质的分布.....	52
3.3.2 楚科奇海胶体有机物的粒径分布.....	53
3.4 讨论.....	58
3.4.1 楚科奇海 CDOM 粒级分布特征.....	58
3.4.2 楚科奇海盐跃层高 CDOM 的形成机制.....	58

3.4.3 楚科奇海 CDOM 的主要来源.....	60
3.5 结论.....	65
<b>第 4 章 夏季大亚湾胶体组成及其粒径分布特征 .....</b>	<b>66</b>
4.1 引言.....	66
4.2 样品采集与分析.....	68
4.2.1 大亚湾环境概况.....	68
4.2.2 样品采集.....	70
4.2.3 样品分析.....	70
4.3 结果.....	70
4.3.1 温度、盐度和 pH 值.....	70
4.3.2 初级生产力.....	76
4.3.3 DOC 的分布.....	77
4.3.4 CDOM 的空间分布.....	78
4.3.5 CDOM 的荧光光谱特征.....	80
4.3.6 胶体有机物荧光强度的粒径分布.....	82
4.4 讨论.....	83
4.4.1 CDOM $a_{254}$ 指示 DOC 的可行性分析.....	83
4.4.2 基于荧光组分的胶体有机物物源分析.....	85
4.4.3 CDOM 吸光光谱斜率及其讨论.....	89
4.5 结论.....	92
<b>第 5 章 结语.....</b>	<b>93</b>
5.1 主要结论.....	93
5.2 特色与创新.....	94
5.3 不足和展望.....	94
<b>参考文献.....</b>	<b>95</b>
<b>附录.....</b>	<b>113</b>

参加的科研项目.....	113
参加的航次.....	113
发表的论文.....	113
致谢.....	115

厦门大学博硕士论文摘要库

## Contents

Abstract(Chinese) .....	V
Abstract(English) .....	XI
Abbreviation .....	XIII
Chapter 1 General introduction .....	1
1.1 Biogeochemical behavior of marine colloidal organic matter .....	1
1.2 Concentration and separation of marine colloidal organic matter .....	4
1.2.1 Ultrafiltration .....	4
1.2.2 Solid-phase extraction .....	7
1.2.3 Reverse osmosis-electrodialysis .....	8
1.3 Detection of marine colloidal organic matter .....	10
1.3.1 Optical spectrum .....	10
1.3.2 NMR and FTI-CR-MS .....	14
1.4 Application of AF4 in marine science .....	14
1.5 Objectives and contents of this study .....	16
Chapter 2 Methods .....	17
2.1 Stirred cell ultrafiltration .....	17
2.2 Retention efficient of stirred cell ultrafiltration .....	18
2.3 Introduction of asymmetric flow field-flow fractionation .....	19
2.4 Size-fractionation principle of asymmetric flow field-flow fractionation .....	24
2.4.1 Laminar flow .....	24
2.4.2 Einstein-Stokes Equation .....	24
2.4.3 Profile of laminar flow rate in the AF4 .....	25
2.4.4 Diffusion model of molecule .....	27
2.5 Refit of injection loop and pressure tube .....	29
2.6 Preconcentration methods .....	31

2.7 Selection of AF4 system parameters.....	33
2.7.1 Carrier solution.....	33
2.7.2 Standards for calibration of the size distribution.....	34
2.8 Linear responses of detector and repeatability tests of samples .....	37
2.8.1 Parallelity test of the UV-Vis absorption detector .....	37
2.8.2 Measurement repeatability of colloidal samples .....	37
2.8.3 Detect limits of the detectors.....	39
2.8.4 Integrated methods of the size distribution curves.....	40
2.9 Methods for size distribution of colloidal organic matter using AF4 .....	42
2.10 Measurements of other parameters .....	44
2.10.1 Absorption spectrum.....	44
2.10.2 EEMs spectrum .....	45
2.10.3 DOC concentration.....	45
2.11 Conclusions.....	46
<b>Chapter 3 Compositions and size distribution of colloidal organic matter</b>	
<b>in the Chukchi Sea .....</b>	<b>47</b>
3.1 Introduction.....	47
3.2 Sampling and analysis.....	49
3.2.1 Sampling.....	49
3.2.2 Preconcentration of the colloidal organic matter.....	49
3.2.3 Methods .....	51
3.3 Results.....	52
3.3.1 Distribution of hydrology, DOC and CDOM optical characteristics in	
the R section .....	52
3.3.2 Size distribution of the colloidal organic matter in the Chukchi Sea.	53
3.4 Discussion .....	58
3.4.1 Size distribution of colloidal organic matter in the Chukchi Sea.....	58

3.4.2 Formation mechanism of high CDOM concentration in halocline in the Chukchi Sea.....	58
3.4.3 Sources of CDOM in the Chukchi Sea.....	60
3.5 Conclusions.....	65
Chapter 4 Compositions and size distribution of colloidal organic matter in Daya Bay in summer .....	66
4.1 Introduction.....	66
4.2 Sampling and analysis.....	68
4.2.1 Introduction of the environments in the Daya Bay .....	68
4.2.2 Sampling.....	70
4.2.3 Analysis .....	70
4.3 Results.....	70
4.3.1 Temperature, salinity and pH value.....	70
4.3.2 Primary production.....	76
4.3.3 Distribution of DOC.....	77
4.3.4 Distribution of CDOM .....	78
4.3.5 Characteristics of CDOM fluorescent spectrum .....	80
4.3.6 Size distribution of fluorescent colloidal organic matter .....	82
4.4 Discussion.....	83
4.4.1 Feasibility of the CDOM $a_{254}$ as an indicator of DOC .....	83
4.4.2 Source of the colloidal organic matter .....	85
4.4.3 Absorption spectra slope of CDOM.....	89
4.5 Conclusions.....	92
Chapter 5 Summary .....	93
5.1 Main conclusions .....	93
5.2 Innovation .....	94
5.3 Shortages and prospects.....	94

References.....	95
Appendixes .....	113
Acknowledge .....	115

厦门大学博硕士论文摘要库

## 摘要

本研究对非对称流场场流仪分离、测量海水中胶体有机物的方法进行了摸索和优化,并通过两个夏季航次的采样和分析,首次开展了楚科奇海和大亚湾胶体有机物光学性质及其粒径分布的研究,进而揭示楚科奇海和大亚湾胶体有机物的来源、组成等信息,获得如下主要认识:

(1) 建立了非对称流场场流仪分离、测量海水胶体有机物的方法,优化了样品进样体积,确定了以 0.9% NaCl 溶液作为分离海水胶体物质的载液;通过多次重复试验确定了最佳的粒径分离方案,评估了光学探头检测平行性、精密度和检出限;确定了采用蛋白类物质作为粒径校正的标准物质,可较准确地获得天然海水胶体有机组分的分子量。

(2) 首次开展了楚科奇海胶体有机物光学性质及其粒径分布的研究,发现三种粒径大小的胶体有机物(1~10 kDa、10~100 kDa 和 >100 kDa) 均与海水中的河水组份份额呈现良好的线性正相关关系,且随着粒径的增加,相关关系有所减弱,证明楚科奇海胶体有机物主要来自陆源输入,而且小分子量组份受陆源输入的影响更为显著。此外,吸光系数  $a_{254}$  是楚科奇海指示陆源有机物输入的良好指标。

(3) 夏季大亚湾海域的 CDOM 含量呈现出湾内高,湾外低的空间分布规律。根据三维荧光光谱的分析结果,大亚湾胶体态 CDOM 的来源主要来自陆源输入、人类排放和当地生物生产过程,其中陆源输入占 50.1%,人类排放输入占 32.8%,生物生产贡献 17.1%。因此,尽管大亚湾是一个生产力较高的沿岸海域,但其有机物还是以陆源输入和人为输入为主。当地生物生产提供的类蛋白组份虽然只占荧光有机物的 17%,但它对大亚湾海域 DOC 的空间变化有较大的影响,导致在大亚湾海域并未观察到 CDOM  $a_{254}$  与 DOC 浓度之间的线性正相关关系,与其他很多海域不同。因此,CDOM  $a_{254}$  不适宜作为指征大亚湾 DOC 变化的指标。另外,大亚湾 CDOM 光谱斜率 ( $s_{210-260}$ ) 与胶体态 CDOM 分子量之间不存在显著的相关关系,因而光谱斜率 ( $s_{210-260}$ ) 也无法反映大亚湾有机组分的粒径

变化。

**关键词：**非对称流场场流仪；有色溶解有机物；胶体有机物；楚科奇海；大亚湾

厦门大学博硕士论文摘要库

## Abstract

The separation and analysis method for marine organic colloids by Asymmetric Flow Field-Flow Fractionation (AF4) was optimized in this study. The properties and size spectra of colloidal organic matter in the Chukchi Sea and the Daya Bay in summer were firstly studied for elucidating the source and composition of colloidal organic matter. The main conclusions were obtained as follows.

(1) The separation and analysis method for marine colloidal organic matter by AF4 was set up with the injected volume being optimized and a solution of 0.9% NaCl used as a carrier. After a series of pre-experiments, proteins with macromolecules were used as the standards to calibrate size spectra of marine colloidal organic matter. Additionally, the repeatability and detection limit of our method were assessed.

(2) All of the integrated CDOM  $UV_{254}$  of three fractions (1~10 kDa, 10~100 kDa, >100 kDa) showed significant correlation with the fraction of meteoric water ( $f_{mw}$ ), and the correlation coefficients decreased with the increasing molecular weights, which indicated the CDOM in the Chukchi Sea was mainly terrigenous and the smaller colloids were more influenced by terrestrial input. Additionally, CDOM  $a_{254}$  is a potential good tracer for terrigenous dissolved organic matter in the Chukchi Sea.

(3) The spatial distribution of CDOM showed a offshore decrease in the Daya Bay in summer. The colloidal CDOM was mainly input from terrestrial, anthropogenic and *in situ* production based on the fluorescent EEMs, with fractions of 50.1%, 32.8% and 17.1% for the terrestrial input, anthropogenic discharge and *in situ* production, respectively. Although the *in situ* production contributed only 17% of fluorescent DOM, it influenced the CDOM distribution, and broken the linear correlation between  $a_{254}$  and DOC in the Daya Bay. Therefore, CDOM  $a_{254}$  is not

suitable for tracing DOC in the Daya Bay. The spectral slope ( $s_{210-260}$ ) showed no significant correlation with the molecular weights of CDOM in the Daya Bay, which ruled out the possibility to use spectral slope ( $s_{210-260}$ ) as an indicator of size change of colloidal organic matter in the Daya Bay.

**Key Words:** Asymmetric flow field-flow fractionation; Chromophoric dissolved organic matter; Colloidal organic matter; Chukchi Sea; Daya Bay

厦门大学博硕士学位论文摘要库

## 缩略词

缩略词	全称	中文名
BSA	Bovine Serum Albumin	牛血清蛋白
CDOM	Chromophoric Dissolved Organic Matter	有色溶解有机物
DIC	Dissolved Inorganic Carbon	溶解无机碳
DOC	Dissolved Organic Carbon	溶解有机碳
EEMs	Excitation-Emission Matrices	荧光矩阵光谱
FDOM	Fluorescence Dissolved Organic Matter	荧光溶解有机物
FFF	Field Flow Fractionation	场流仪
FTIR	Fourier Transform Infrared Spectroscopy	傅里叶变换红外谱
kDa	kilo-Dalton	千道尔顿
LDOM	Labile Dissolved Organic Matter	易降解溶解有机物
M.W.	Molecular Weights	分子量
NMR	Nuclear magnetic resonance spectroscopy	核磁共振谱
PARAFAC	Parallel Factors Analysis Program	平行因子分析程序
POM	Particulate Organic Matter	颗粒有机物
PSS	Polystyrene Sulfonate	聚苯磺乙烯
RDOM	Refractory Dissolved Organic Matter	难降解溶解有机物
RO/ED	Reverse Osmosis-Electro-Dialysis	反渗透-电渗析
SPE	Solid-Phase Extraction	固相萃取技术
TOC	Total Organic Carbon	总有机碳
$s_{275-295}$	Spectrum slope between 275 nm and 295 nm	275 nm-295 nm 之间的 光谱斜率
$s_R$	Slope ratio at $s_{275-295}$ and $s_{350-400}$	斜率比值
VB <sub>12</sub>	Vitamin B <sub>12</sub>	维他命 B <sub>12</sub>

Degree papers are in the “[Xiamen University Electronic Theses and Dissertations Database](#)”.

Fulltexts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to [etd@xmu.edu.cn](mailto:etd@xmu.edu.cn) for delivery details.