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——庆祝厦门大学环境学科创立40周年



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海水痕量营养盐和金属的分子光谱分析方法研究进展

袁东星, 黄勇明, 王婷

(厦门大学环境与生态学院, 近海海洋环境科学国家重点实验室, 厦门 361102)

摘要: 海洋现场观测是获取海洋环境研究数据的重要途径. 鉴于海洋的现场环境严酷复杂, 以及采集、储存和运输海水样品的困难, 海洋化学参数的现场和原位检测一直为海洋学家所追求, 成为海水分析技术的研究热点. 通过综述近年来海水痕量营养盐和重要痕量金属的分子光谱分析方法的研究进展, 从灵敏度和测定范围等方面, 总结痕量营养盐(活性磷、亚硝氮、硝氮、铵态氮)和痕量金属(铁、锰、铜、铝)的分析技术, 侧重于现场和原位测定方法, 聚焦于分光光度法、荧光法和化学发光法等适用于海洋现场的光学检测方法的研究情况, 同时展示这些方法及相应仪器在岸基实验室、船基实验室、海洋走航分析以及原位长期观测中的应用实例; 并对现存的关键问题及可能的解决方案进行探讨, 对本领域今后的发展方向做出展望.

关键词: 海水; 营养盐; 金属; 分子光谱法; 痕量分析

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Research Progress of Analytical Methods with Molecular Spectroscopy for Determination of Trace Nutrients and Metals in Seawaters

YUAN Dong-xing, HUANG Yong-ming, WANG Ting

(State Key Laboratory of Marine Environmental Science, College of the Environment and Ecology, Xiamen University, Xiamen 361102, China)

Abstract: On-field monitoring is an important way to obtain data in marine environmental research. The ocean environmental conditions are harsh and complex, and there are many difficulties in seawater sample collecting, storing, and transporting. Therefore, the on-field and in-situ detections of chemical parameters have always been pursued by oceanographers and have become a research hot point in the seawater analysis field. In this review, the recent research progress of detection methods with molecular spectroscopy techniques for trace nutrients and metals in seawater was summarized. From the view of sensitivity and detection range, we discussed analytical techniques of trace nutrients (phosphate, nitrate, nitrite, and ammonium) and metals (iron, manganese, copper, and aluminum). It focused on methods of on-field and in-situ measures and development of optical methods such as spectrophotometry, fluorescence, and chemiluminescence, as well as the corresponding instruments that are most suitable in marine field observation. Examples of the application of these methods and relative instruments in land-and ship-based laboratories, ship-board underway monitoring, and long-term in-situ observation were presented. The key problems and possible solutions were analyzed, and the future development of the research field was proposed.

Key words: seawaters; nutrients; metals; molecular spectroscopy; trace analysis

海洋浮游植物的初级生产力占地球总初级生产力的一半^[1]. 营养盐, 指的是浮游植物生长必需的活性磷、亚硝酸盐氮(亚硝氮)、硝酸盐氮(硝氮)、铵盐氮(铵态氮)和活性硅等主要营养元素. 海洋中氮的生物地球化学循环是地球系统中最重要的一环之一^[2]. 在长时间尺度上, 磷被认为是最终限制性营养元素^[3]. 海洋中的活性硅因含量较高, 引发的限制现象很少, 因而不受关注. 经检索, 2005年至今仅有研究报道了海水中痕量硅酸盐的测定^[4-6], 且均基于经典的硅钼蓝分光光度法, 故本综述不做专门论述. 除了营养盐, 海洋浮游植物的生长还离不开铁、锰和铜等痕量营养元素^[7]. 铝并非重金属, 却是多种海洋生物地球化学过程的示踪元素^[8], 因而亦被重视.

大洋表层海水中营养盐和营养元素的浓度极低且形态易变, 要求分析方法拥有高灵敏度和选择性. 准确获取海水中这些物质的浓度数据, 是海洋生物地球化学和生态研究的基础.

本文主要综述 2005 年以来海水痕量营养盐和痕量金属的现场和原位分子光谱检测法及仪器的研

发进展, 亦引用了少量 2005 年之前的经典或极具代表性的文献.

1 通用检测技术和仪器

海洋环境的复杂和险恶, 导致很多分析仪器无法应用于船基实验室或海水水体. 分子光谱法是少数几种在海洋现场“不晕船”的方法之一, 其中以分光光度法、荧光光度法和化学发光法应用最广, 红外光谱法和拉曼光谱法的应用很少. 此外, 电化学分析中的电势分析法在海洋环境监测中亦有所应用, 但不在本文的讨论范围内. 本文所述的“现场”, 指在船基或渔排上; 所述的“原位”, 指在水体中.

1.1 流动分析技术

在现场和原位分析场合, 自动化分析方法和仪器越来越受青睐, 其中以流动分析(flow analysis, FA)技术最为瞩目. FA 包括气泡间隔连续流动分析

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作者简介: 袁东星(1955~), 女, 教授, 主要研究方向为海洋环境监测技术, E-mail: yuandx@xmu.edu.cn

(segmented continuous flow analysis, SCFA)^[9]、流动注射分析(flow injection analysis, FIA)^[10]、连续流动分析(continuous flow analysis, CFA)、顺序注射分析(sequential injection analysis, SIA)^[11]和阀上实验室(lab-on-valve)^[12]等. FA 在几十年里得到了迅速发展,广泛地应用于海水分析中^[13,14].

FA 的特点是操作简单、自动化程度高、重现性好、分析速度快和外界污染风险低^[13,15]. 将 FA 与分子光谱法联用,是现场分析和原位分析的理想手段,成为目前海水营养盐自动测定仪器的主流^[13,14].

1.2 固相萃取和长光程技术

测定营养盐和营养元素含量在 $\text{nmol}\cdot\text{L}^{-1}$ 级别的水样,常规分光光度法的灵敏度远不能满足要求. 用于提高灵敏度的技术通常有两种,一种是固相萃取(solid phase extraction, SPE),另一种是液芯波导毛细管流通池(liquid waveguide capillary cell, LWCC)^[16]. 在目前流行的海水痕量分析中,这两种技术通常分别或联合与上述的 FA 联用.

SPE 可从大体积水样中富集痕量目标物或其衍生物,较常见的方法是在线富集生成的衍生物,再检测此浓缩的衍生物. 商品化的离子交换树脂、C18 或亲水亲脂平衡(HLB)小柱是 FA 体系中最常用的富集元件. SPE 柱的使用包括活化、上样、淋洗和洗脱这 4 个步骤,洗脱后的浓缩试液可用分光光度法和荧光光度法测定. SPE 法可将目标物与基底分离,消除基底尤其是盐效应的干扰;但样品需求量较大,步骤较多,测定时间较长.

LWCC 是提高灵敏度的另一种技术,也称长光程法,用于分光光度检测. 由 Lambert-Beer 定律可知,增加光程可提高方法灵敏度. 但由于光衰减和死体积大等原因,常规流通池的光程一般小于 10 cm. 1989 年,美国杜邦公司发明了折射率小于水的氟塑料 Teflon AF1600 (折射率 1.31) 和 Teflon AF2400 (折射率 1.29)^[17],用其制成的细长流通管称为 LWCC. 当充满水溶液之后,光可在内壁发生全反射,在光损失很小的情况下极大地增加了光程. 理论上,采用 1 m 长的 LWCC,可将灵敏度提高 1~2 个数量级. 基于 LWCC 的 FA 流路较简单,样品需要量小,测样速度快,但也存在若干不足:在提高目标物吸光值的同时增加了试剂空白;易受 Schlieren 效应^[18]影响;流路中若有气泡不易排除;且 LWCC 易堵塞,吸附在内壁的物质难以清洗.

2 营养盐测定

近岸海水营养盐的现场、原位测定方法和仪器已经相当成熟. 监测仪器的产业主要分布在欧美国

家,代表性公司有:美国 EnviroTech 公司^[19]、美国 Sea-Bird 电子公司^[20]、英国的 ClearWater Sensors^[21] 和意大利 Systea S. p. A. 公司^[22]等. 值得注意的是,有相当一部分企业(如美国 YSI 公司^[23])并非仅生产海洋专用仪器,所产的水环境监测仪器基本上可以通用于近岸海洋环境监测. 在检测指标方面,EnviroTech 公司仪器的硝氮、铵态氮和活性磷的检出限均为 $3\ \mu\text{g}\cdot\text{L}^{-1}$; CleanWater Sensors 公司的仪器检出限,硝氮为 $25\ \text{nmol}\cdot\text{L}^{-1}$,活性磷为 $40\ \text{nmol}\cdot\text{L}^{-1}$,铁为 $20\ \text{nmol}\cdot\text{L}^{-1}$. 由于近海环境中营养盐的含量较高,上述性能指标已能满足监测要求.

然而,在开阔海洋特别是一些寡营养盐海域中,营养盐被浮游植物大量摄取,表层浓度低至 $\text{nmol}\cdot\text{L}^{-1}$ 水平,低于常规分析方法的检出限. 为了获取研究数据,科学家极需要灵敏的方法和仪器. 而对于仪器厂家来说,这类仪器的技术指标要求苛刻,产品需求量小,研发机会成本高,故缺乏研发动力. 因此,科学家们寄希望于研究型的痕量分析方法和仪器,并为此付出不懈努力.

2.1 活性磷

活性磷的测定一般采用磷钼蓝分光光度法,这也是我国海水分析的标准方法^[24,25] 和美国 EPA^[26] 的推荐方法. 将磷钼黄还原为磷钼蓝的常用还原剂有氯化亚锡和抗坏血酸^[27~34]. 使用氯化亚锡还原的方法易受氯离子干扰,因此不适用于海水分析. 抗坏血酸还原法在催化剂酒石酸锑钾存在下,受硅酸盐的干扰少,稳定时间长^[24],因而在海水分析中广泛使用. 也可选择直接测定未经还原的磷钼黄,但方法灵敏度较低^[35~37]. 除磷钼蓝分光光度法外,利用染料与磷钼杂多酸生成离子缔合物的 FA 方法见文献^[38~41].

海水中活性磷测定以 FA 结合分光光度法为主,也有研究者采用荧光光度法^[42,43] 和化学发光法^[44]. 鲁米诺化学发光法的灵敏度高,但大多用于淡水中磷酸盐的分析,在分析海水样品时,容易受到钙镁等共存离子的干扰^[44]. 还有采用原子光谱和质谱法的,但并不普遍. 目前,提高灵敏度的主要方法是富集法和长光程法^[16]. 表 1 汇总了近年来基于磷钼蓝的海水活性磷测定法.

2.2 亚硝氮和硝氮

测定亚硝氮和硝氮的分子光谱方法主要是衍生-可见分光光度法,其也是推荐的标准方法^[24~26]. 此外还有荧光分光光度法^[53,54] 和化学发光法^[55~57]等. 化学发光法易受其他离子干扰,一般用于地表水中的亚硝氮和硝氮分析. 2008 年, Patey 等^[58] 曾对 $\text{nmol}\cdot\text{L}^{-1}$ 级别的海水硝氮和活性磷的测定做了综述.

表 1 以磷钼蓝法为基础的海水活性磷测定方法和应用

Table 1 Methods for determination of phosphate in seawaters based on phosphomolybdenum blue method and their application

分析技术要点 ¹⁾	检出限 /nmol·L ⁻¹	测定范围或上限 /nmol·L ⁻¹	方法应用	文献
表面活性剂, FIA-SPE(C18)	1.57	3.2~48.5	实验室测定大洋海水	[44]
FA, 0.5 m LWCC		1~1 000	原位观测寡营养盐海域上层 200 m	[45]
表面活性剂, FIA-SPE(C18), 改进型	1.57	3.4~515 (不同工作曲线)	船上测定南海 200 多个水样	[27]
SIA-SPE(HLB)	1.42	3.4~1 134 (不同工作曲线)	实验室测定南海剖面水样	[28]
MAGIC 法, CFA-2 m LWCC	0.3	25	实验室测定海水样	[46]
FIA-2 m LWCC	1.5	100	北大西洋走航测定 1 000 多个水样	[47]
rFIA-2 m LWCC	0.5	8~165	实验室测定南海水样	[33]
双通道 SIA	7	0.024~9.5 μmol·L ⁻¹	实验室测定河口水样	[29]
SIA, 标准加入法	340	14.8~73.9 μmol·L ⁻¹	实验室测定河口和近岸海水样	[34]
SCFA-2.5 m LWCC	0.8	250	GEOTRACES 2010 航次走航分析	[48]
FA, 环流分析	32	50 μmol·L ⁻¹	实验室测定海水样	[16]
SPE(HLB), 手工操作	3.0	0.9 μmol·L ⁻¹	实验室测定 42 个西太平洋水样	[49]
颗粒态磷, 过滤-氧化-酸提-1 m LWCC	0.3	1 μmol·L ⁻¹	实验室测定南太平洋水样	[50]
FIA-常规光谱仪	74	0.65~6.5 μmol·L ⁻¹	实验室分析河口水样	[31]
CFA-SPE(HLB)	1.0	80	南海走航测定 2 000 余个水样	[32]
SCFA-1 m LWCC	4	1 μmol·L ⁻¹	实验室测定太平洋水样	[51]
表面活性剂, pFI-CFA	32	3 μmol·L ⁻¹	实验室测定海水样	[52]

1) FIA: 流动注射分析, SPE: 固相萃取, FA: 流动分析, LWCC: 液芯波导毛细管流通池, SIA: 顺序注射分析, HLB: 亲水亲酯平衡, MAGIC: 氮氧化镁共沉淀法, CFA: 连续流动分析, rFIA: 反相流动注射分析, SCFA: 气泡间隔流动分析, pFI: 编程流动注射

最经典的亚硝氮的衍生测定是基于重氮偶联反应的 Griess 法^[59]. 而硝氮的测定通常通过测定硝酸盐还原生成的亚硝酸盐来间接进行, 原始样品中亚硝氮浓度与硝酸盐还原后样品中总亚硝氮浓度之差, 即为硝氮浓度.

还原硝氮常用的方法有锌还原法^[60]、锌镉还原法^[24,25]和铜镉还原法^[25,26,47,61,62]等. 铜镉还原法因还原效率高, 最为常用. 由于镉具有一定的毒性, 且在 FA 中使用固态镉柱不甚方便, 近年来, 研究者们尝试采用三氯化钛溶液还原硝氮和亚硝氮为氮氧化物^[57], 以及采用三氯化钒溶液还原硝氮为亚硝氮^[63,64].

洁净海水中较高浓度的硝氮可以在深紫外光区直接测定^[65,66]. 近年来有研究基于算法测定硝氮^[67,68], 先获取深紫外光区的原始吸收光谱, 再用算法解析光谱. 拉曼光谱法偶尔也应用于同时测定深海热液口的硝氮、硫酸根和碳酸根, 硝氮的测定范围为 0.12~0.34 g·L⁻¹^[69].

表 2 汇总了近年来海水中痕量亚硝氮和硝氮的分子光谱测定方法.

2.3 铵态氮

铵态氮的测定一般基于分光光度法或荧光法. 分光光度法又有纳氏试剂法 (Nessler's reagent) 和靛酚蓝法 (indophenol blue, IPB) 之分. 纳氏试剂法受盐度干扰, 一般应用在地表水、地下水、生活污水和工业废水的铵态氮测定中. 靛酚蓝法是海

水中铵态氮测定的标准方法^[25,26], 优点是简单、易于实现自动化且不受有机胺干扰; 缺点是显色反应时间较长, 灵敏度较低. 基于采用的试剂, 靛酚蓝法又分为水杨酸-次氯酸盐分光法和苯酚-次氯酸盐分光法.

荧光法则使铵态氮与邻-苯二甲醛 (o-phthalaldehyde, OPA) 和还原试剂 (巯基乙醇、硼氢化物或亚硫酸盐) 反应, 产生强荧光物质异吲哚衍生物. 1997 年, 亚硫酸盐还原体系首次用于海水铵态氮的分析^[78]. 荧光法的灵敏度虽然较高, 但有机胺的干扰不容忽视. 研究表明, 不同有机胺的干扰程度不一, 当亮氨酸等氨基酸与铵态氮浓度比为 1:1 时, 铵态氮的荧光信号将下降约 45%^[79]. 因此, 荧光法更适用于寡营养盐海域.

化学发光法利用铵与次氯酸根的反应产物能降低鲁米诺发光强度的原理测定铵态氮^[80,81]. 此方法简单、灵敏且快速, 但易受到海水基底干扰, 一般需要辅以一定的分离手段.

融合了 FA 技术的测定方式在铵态氮测定中广泛使用. Li 等^[82]提出的 SCFA-LWCC-IPB 法是较早地将 LWCC 应用于测定海水痕量铵态氮的方法, 使用 1 m LWCC, 方法检出限为 5 nmol·L⁻¹. 结合 SPE 技术提高灵敏度的方法亦见文献^[83,84].

把铵态氮与复杂基底分离, 再结合其他手段进行测定, 也是铵态氮现场分析常用的方法. 将水样与碱性溶液混合, 使铵态氮转化为气态氨逸出, 透过气

表 2 海水亚硝氮和硝氮的分子光谱测定方法和应用¹⁾

Table 2 Spectrophotometric methods for determination of nitrite and nitrate in seawaters and their applications

分析技术要点	目标物	检出限 /nmol·L ⁻¹	测定范围或上限 /μmol·L ⁻¹	应用	文献
UV 200-300 nm 直接测定	硝氮	0.2 ~ 1 500		海底, 3 ~ 6 个月连续测定	[69]
CFA-97 cm LWCC	亚硝氮	1	1.0 ~ 500 nmol·L ⁻¹	原位观测上层 200 m	[70]
间苯二酚	硝氮	500	0.5 ~ 400 nmol·L ⁻¹	实验室测定北大西洋剖面水样	[71]
UV 205, 212 nm 直接测定	亚硝氮, 硝氮		0.71 ~ 429	原位观测河口	[65]
CFA-15 cm LWCC	硝氮	2	0.002 ~ 20	原位观测寡营养盐海域上层 200 m	[45]
SIA-SPE(C18)-2 cm 流通池	亚硝氮	0.1	0.71 ~ 42.9 nmol·L ⁻¹	船上测定南海剖面海水样	[72]
FIA-2 m LWCC	硝氮 + 亚硝氮	0.3	200 nmol·L ⁻¹	北大西洋走航测定 1 000 多个水样	[47]
SIA 亚硝氮 2 cm, 硝氮 1 cm 池	亚硝氮 硝氮	110 3 700	0.50 ~ 8.00 12.5 ~ 305	实验室测定河口水样	[61]
FIA-SPE(HLB)-16 cm LWCC	亚硝氮 硝氮	0.3 1.5	1 ~ 100 nmol·L ⁻¹ 5 ~ 200 nmol·L ⁻¹	实验室测定南海水样	[73]
SIA-SPE(HLB)-2 cm 池	亚硝氮	0.5	1.4 ~ 85.7 nmol·L ⁻¹	实验室测定南海水样	[74]
rFIA, 锌粒还原, 1.7 cm 池	硝氮	92	0.21 ~ 50	走航测定 3 200 个水样	[60]
阀上芯片, 2.5 cm 池	亚硝氮 硝氮	30 100	14.5 23.5	实验室测定西班牙海湾水样	[62]
FA, 环流分析, 改进型	亚硝氮	20	10	实验室测定近岸海水样	[75]
化学发光, Ti(III) 还原	亚硝氮 + 硝氮	0.45	1 ~ 1 000 nmol·L ⁻¹	实验室测定夏威夷海水样	[57]
便携式 rFIA-荧光仪	亚硝氮	10	7	描绘墨西哥近岸“三氮”图	[54]
	亚硝氮 + 硝氮	22	9		
	铵态氮	11	4		
无阀 CFA	亚硝氮	60	40	河口及近岸走航分析	[76]
	硝氮	270	180		
	活性磷	80	14		
SIA-VCl ₃ 还原, 亚硝氮 3 cm 池, 硝氮 1 cm 池	亚硝氮	20	100	河口和近岸走航分析	[64]
	硝氮	140	400		
pFI, 50 cm 直线路程	亚硝氮	1.9		实验室测定海水样	[77]
rFIA-VCl ₃ 还原	硝氮	30	7.5	河口和近岸走航分析	[63]

1) 若无特别标注, 测定方法为重氮偶联-可见分光光度法; 其余同表 1

体扩散 (gas diffusion, GD) 装置^[85] 或吹扫-捕集 (purge and trap, P&T) 装置^[86], 再由溶液吸收, 实现基底分离. 吸收液若是酸性溶液, 可用电导检测器检测电导率的变化; 若是酸碱指示剂, 则可由分光光度法检测指示剂吸光值的变化^[87,88]. 气体逸出法可以与分光光度法^[89,90]、荧光光度法^[86] 和化学发光法^[80] 等联用, 优点是基本无基底干扰, 缺点是扩散效率低, 分析时间长.

已报道的铵态氮分析方法研究和应用实例很多. 2019 年, Zhu 等^[91] 对 1999 ~ 2019 年的 20 年间海水铵态氮的各种分析方法进行了详细的综述, 并分类列表汇总. 因此, 表 3 仅列举近 10 年来海水铵态氮的分子光谱分析实例.

3 痕量金属测定

测定海水痕量金属, 陆基实验室通常采用石墨炉原子吸收光谱法和电感耦合等离子体-质谱法; 现场分析主要是电化学法和光学法; 而连续走航分析和原位分析, 主要是分子光谱法. 分子光谱法包括络合衍生分光光度法、催化分光光度法和化学发光法.

3.1 铁

海水中铁的价态包括 Fe(II) 和 Fe(III). 铁的含量极低, 主要利用富集或长光程手段, 结合 FA 技术和分光光度法或化学发光法进行测定, 也有利用荧光淬灭的方法间接检测 Fe(III)^[104,105]. 分光光度法分为络合衍生分光光度法和催化分光光度法两类.

铁的络合衍生显色试剂有: 1,10-菲啰啉^[106]、咪喃三嗪二钠 (Ferene)^[107] 和菲咯嗪^[106,108-110] 等. 其中, 菲咯嗪对 Fe(II) 的灵敏度和选择性均好, 自 1970 年由 Stookey^[111] 报道之后, 就被广泛应用于铁的氧化还原形态测定. Fe(III) 可在短时间内被抗坏血酸还原为 Fe(II), 故基于菲咯嗪显色反应的方法亦可分析 Fe(II + III). 采用 LWCC 或 SPE 小柱富集的方法均可降低检出限. 络合衍生分光光度法的检出能力为 nmol·L⁻¹ 级别, 可满足河口水、近岸海水中铁的检测需求. 早在 1991 年, Coale 等^[112] 就将此法用于海底热液区铁和锰的原位测定.

铁在 pH 5.5 ~ 6.0 的弱酸介质中可显著催化 N,N'-二甲基对苯二胺 (N,N'-dimethyl-p-

表 3 海水铵态氮的分子光谱测定方法和应用¹⁾

Table 3 Spectrophotometric methods for determination of ammonium in seawaters and their applications

测定原理	分析技术要点	检出限 /nmol·L ⁻¹	线性范围或上限 /μmol·L ⁻¹	应用	文献
OPA 荧光	便携式荧光检测器	10	0.05 ~ 10	海港原位应用	[79]
OPA 荧光	序批式 SPE (HLB)	1.2	1.67 ~ 300 nmol·L ⁻¹	船上测定南海水样	[84]
IPB-苯酚-分光	FIA-2.5 m LWCC	3.6	0.01 ~ 30	船上测定近岸海水水样, 实验室测定南海水样	[92]
合成新荧光试剂 + 亚硫酸盐	手动, 普通荧光仪测定	5.8	0.03 ~ 0.30	实验室测定南海水样	[93]
IPB-苯酚-分光	SFA-GD-1 m LWCC	630 nm: 5.5 530 nm: 13	630 nm: 1 530 nm: 10	船上测定黑潮海水水样	[94]
IPB-OPP 分光	SFA-LWCC	1 m: 6 2 m: 4	0.20	南太平洋走航分析	[95]
OPA 荧光	FIA-P&T	7.4	0.01 ~ 0.40	实验室测定南海水样	[96]
分光法	SIA, 顶空-单滴微萃取	1800	25	实验室测定近岸海水水样	[97]
GD-指示剂溴百里酚蓝-分光	FIA	2 mL: 15 1 mL: 88	0.028 ~ 5.6 0.028 ~ 13.9	实验室测定河口和近岸海水水样	[88]
IPB-OPP-分光	1 cm 池	200	100	实验室测定近岸和南海水样	[98]
IPB-OPP-分光	rFIA	80	35	实验室测定河口和近岸海水水样	[99]
OPA + 亚硫酸盐 + 甲醛-荧光	FIA, 自制荧光检测器	2.1	0.30	河口和近岸走航分析	[100]
合成新荧光试剂 + 亚硫酸盐	手动, 荧光检测器, 单、双激光二极管	单: 6.5 双: 3.5	单: 5 双: 2	实验室测定海水水样	[101]
IPB-OPP-分光	SIA, 3 cm 池	150	200	福建近岸走航分析	[102]
荧光法	SIA-P&T	57	0.19 ~ 11	实验室测定河口水和海水水样	[86]
OPA-荧光	FIA-SPE (HLB)	2	1.2	近岸走航分析, 船上测定南海剖面水样	[103]

1) OPA: 邻-苯二甲醛, IPB: 靛酚蓝, OPP: 邻苯基苯酚, GD: 气体扩散, P&T: 吹扫-捕集, 其余同表 1

phenylenediamine, DPD) 被 H₂O₂ 氧化显色的反应^[113], 利用此建立的铁催化分光光度法灵敏度很高. 若再与 FA 及 SPE 富集技术联用, 检出限达几十 nmol·L⁻¹, 可用于海水中痕量铁的现场分析和原位观测. 目前常用的富集树脂为次氨基三乙酸 (nitrilotriacetic acid, NTA) 离子交换树脂, 商品名为 NTA Superflow^[114].

基于 Fe(II) 或 Fe(III) 对特定化学发光体系的催化作用, 可建立起高灵敏度的海水痕量铁分析方法. Bowie 等^[115] 研发了 Fe(II) 催化的鲁米诺-O₂ 体系, 对 Fe(II) 的特效性强, 灵敏度极高, 应用于大洋表层和剖面超痕量 Fe(II) 的现场分析, 检出限 21 pmol·L⁻¹, 线性范围 21 ~ 2 000 pmol·L⁻¹.

近年来海水中痕量铁的分子光谱测定方法汇总于表 4 中.

3.2 锰

海水中痕量锰的现场分析方法主要是与 FA 结合的络合衍生分光光度法、催化分光光度法或化学发光法.

甲醛肟最早应用于分析海水中锰的络合衍生分光光度法中^[131], 但方法灵敏度低且受其他离子干扰大. 1-(2-吡啶基偶氮)-2-萘酚 [1-(2-pyridinylazo)-2-naohtalenol, PAN] 分光光度法的灵敏度较高, 但易受铁、锌、铜等金属离子的干扰. 在

近岸和海底热液附近, 锰含量较高且远高于其他金属离子, 因此近岸和海底热液中锰的检测常采用 PAN 分光光度法^[132].

利用锰的催化作用可建立催化分光光度法, 典型的催化反应体系有高碘酸盐氧化隐色孔雀绿 (leucomalachite green, LMG) 的显色反应和过氧化氢氧化钛铁试剂 (Tiron) 的显色反应. 锰催化分光光度法灵敏度高, 但受盐度、pH 和温度等实验条件的影响较大.

早期的典型研究包括: Ólafsson^[133] 首先将 LMG 反应体系与 SCFA 结合, 对海水痕量锰进行自动测定; Resing 等^[134] 将螯合树脂 8-羟基喹啉 (8-hydroxyquinoline, 8-HQ) 小柱引入流路, 在富集的同时抑制海水基底干扰. Mallini 等^[135] 利用 Tiron 反应建立了测定海水痕量锰的 FIA-SPE (8-HQ)-分光光度法.

化学发光法具有极高的灵敏度, 所需仪器简单, 适用于痕量金属的现场分析. 但化学发光法受海水基底干扰较大, 一般需与金属螯合树脂联合使用. 利用 8-HQ、亚氨基二乙酸 (iminodiacetic acid, IDA) 或 NTA 等树脂选择性地富集锰, 再以经典的鲁米诺-H₂O₂ 化学发光法进行检测, 可建立高灵敏度的痕量锰分析方法.

表 5 汇总了近年来海水中痕量锰的典型分子光谱分析法.

表 4 海水中铁的分子光谱测定方法和应用¹⁾

Table 4 Spectrophotometric methods for determination of iron in seawaters and their applications

分析技术要点 ¹⁾	目标物	检出限 /nmol·L ⁻¹	测定范围或上限 /nmol·L ⁻¹	应用	文献
FIA-菲咯嗪分光-3 cm 池	Fe(II) Fe(II + III)	60 70	0.3 ~ 100 μmol·L ⁻¹	原位观测大西洋海底热液区	[108]
菲咯嗪分光-5 m LWCC	Fe(II)			研究痕量Fe(II)的氧化与 pH、碳酸根、温度、盐度的关系	[110]
FIA-DPD 催化分光-3 cm 池	Fe(II)	1.6 0.15(加 SPE(8-HQ))	64 100	原位观测近岸剖面	[116]
FA-SPE(NTA)-催化分光	Fe(II) Fe(III)	nmol·L ⁻¹ 量级		讨论 pH 对富集的影响	[114]
FA-SPE(NTA)-DPD 催化分光	Fe(II) Fe(III)	0.024 0.024		船上测定北太平洋和美国西海岸水样	[117,118]
FIA-鲁米诺/O ₂ -化学发光	Fe(II)	0.05		船上测定北太平洋剖面水样	[119]
FIA-SPE(8-HQ), DPD 催化分光, 3 cm 池	Fe(II + III)	0.025	9	船上测定大西洋水样	[120]
FIA-鲁米诺/O ₂ -化学发光	Fe(II) Fe(II + III)	1 ~ 11 pmol·L ⁻¹ (每日变化)	1.5	船上测定西太平洋剖面水样	[121]
FIA-鲁米诺/O ₂ -化学发光	Fe(II)	0.012	0.125	船上测定太平洋 1452 个剖面水样	[122]
FIA-菲咯嗪, CHEMINI 仪器	Fe(II) Fe(II + III)	300 300	100 μmol·L ⁻¹	原位观测大西洋海底热液	[109]
SIA-1 m LWCC-分光	Fe(II + III)	菲咯嗪: 2.7 邻菲罗啉: 6.3	357	实验室测定海水样	[106]
MSFIA-SPE-菲咯嗪分光-1 m LWCC	Fe(II + III)	NTA: 0.89 Chelex-100: 3.6	142 268	实验室测定标准参考样	[123]
rFIA-DPD 催化分光	Fe(II + III)	0.40	0.8 ~ 230	实验室测定珠江口及近岸海水样	[124]
CFA-Ferene 分光-14 cm 池	Fe(II)	20	0.1 ~ 2.0 μmol·L ⁻¹	原位观测波罗的海缺氧区剖面	[125]
CFA-DPD 催化分光	Fe(II + III)	0.05 ng·g ⁻¹	0.1 ~ 5 ng·g ⁻¹	实验室分析格陵兰冰芯	[126]
rFIA-菲咯嗪分光-2 m LWCC	Fe(II) Fe(II + III)	0.3 0.7	0.5 ~ 250	东海走航分析	[127]
FA-SPE(C18)-菲咯嗪分光-2 m LWCC	Fe(II) Fe(II + III)	0.056 0.096	0.5 ~ 50	现场周日连续测定河口及近岸海水	[128]
微流控-菲咯嗪分光	Fe(II)	27	500	原位观测波罗的海剖面	[129]
pFI	Fe(II)	两种停流方式 10 ~ 55		实验室测定海水样	[130]

1) DPD: N,N-二甲基对苯二胺, NTA: 次氨基三乙酸离子交换树脂, MSFIA: 多注射泵流动注射分析, Ferene: 吠喃三嗪二钠, 其余同表 1

表 5 海水中锰的分子光谱测定方法和应用¹⁾

Table 5 Spectrophotometric methods for determination of manganese in seawaters and their applications

分析技术要点	检出限 /nmol·L ⁻¹	定量范围或上限 /nmol·L ⁻¹	应用	文献
PAN 分光	25	600	AUV 上, 苏格兰西海岸 4 000 多个数据点	[132]
FA-SPE(IDA)-LMG 分光	0.03	40 ~ 100 (不同取样体积)	船上测定加州海岸剖面海水	[136]
微流控-鲁米诺-H ₂ O ₂ 化学发光	10		AUV 或 ROV 上, 探索深海热液区	[137]
催化分光, 人工神经网络, 同时测定铁	μg·L ⁻¹ 量级		实验室测定青岛近岸海水样, 探讨计算结果和标准的偏差	[138]
微流控-鲁米诺-H ₂ O ₂ 化学发光	280	500	ROV 上, 探索冲绳县深海热液区	[139]
FA-PAN-1 m LWCC	3.0	10 ~ 1 500	河口和近岸走航分析	[140]
微流控-PAN 分光, 同时测定铁	28	4.55 μmol·L ⁻¹	原位观测波罗地海剖面	[129]
MSFIA-阀上实验室-Tiron 催化分光-1 m LWCC	0.55	10 ~ 640	实验室测定海水标准样	[141]
METals 原位分析仪 PAN 分光-14 cm 池	77	5 μmol·L ⁻¹	原位观测波罗的海中部剖面	[142]
LMG 催化分光, rFIA-1 m LWCC	0.2	0.50 ~ 10	实验室分析南海剖面水样	[143]
亮柏蓝分光, LWCC	1 m LWCC: Mn(III) 6.7; MnOx 7 pmol·L ⁻¹ 1 cm 池: Mn(III) 260; MnOx 2.6	Mn(III): 200 MnOx: 100	实验室分析西北大西洋河口离岸海水	[144]
阀上实验室-PAN + Triton-X100 分光-3.46 cm 池	27	3 μmol·L ⁻¹	波罗地海西南部原位应用	[145]

1) PAN: 1-(2-吡啶基偶氮)-2-萘酚, LMG: 隐色孔雀绿, Tiron: 钛铁试剂, 其余同表 4

3.3 铜

关于海水中铜的测定报道不多. 同铁和锰的测定一样, 铜的测定主要包括络合衍生分光光度法、催化分光光度法和化学发光法. NTA 树脂^[144]和 8-HQ 树脂^[146]均应用于铜的富集, 以提高方法的灵敏度.

海水中铜(II)的络合衍生分光光度主要基于铜(II)和二乙氨基二硫代甲酸钠(diethyldithiocarbamate, DDTC)的反应. 此法是我国早期海水中铜(II)的标准测定方法^[147], 但灵敏度较低, 操作繁琐, 且所用的有机溶剂毒性大, 故在 2007 年的海洋监测规范中已被删除.

催化分光法利用铜(II)催化某个氧化还原反应的原理测定铜. 这些体系的例子有: 铜(II)催化铁氰化钾氧化柠檬酸^[148]、铜(II)催化铬酸根氧化巯基乙酸和巯基丙酸^[149]. 2019 年, Zhang 等^[150]基于铜(II)催化铁氰化钾氧化谷胱甘肽的特性测定海水中的铜(II), 检出限 $0.625 \text{ nmol} \cdot \text{L}^{-1}$, 线性范围 $3.13 \sim 547 \text{ nmol} \cdot \text{L}^{-1}$. 但以上研究均仍然基于传统的离线手工作业, 操作繁琐, 耗时长, 实验条件不易控制. 至 2022 年, Wang 等^[151]基于铜(II)催化铁氰化钾与谷胱甘肽的褪色反应, 建立了海水中痕量铜(II)的 rFIA-LWCC-催化动力学分光光度法, 检出限 $0.23 \text{ nmol} \cdot \text{L}^{-1}$, 测定上限 $0.025 \mu\text{mol} \cdot \text{L}^{-1}$, 并应用于福建九龙江河口的现场走航观测.

化学发光法基于铜(II)对鲁米诺- $\text{O}_2/\text{H}_2\text{O}_2$ 发光体系的特效性催化作用测定铜(II). 但其受海水基底干扰, 一般需与金属螯合树脂联合使用. Sandford^[146]基于 FIA 技术, 采用 8-HQ 树脂富集海水中的铜(II), 洗脱后用 1,10-菲咯啉-化学发光法测定, 线性范围 $0.1 \sim 50 \text{ nmol} \cdot \text{L}^{-1}$, 检出限 $25 \text{ pmol} \cdot \text{L}^{-1}$, 成功测定了南大西洋和北大西洋表层水中的铜(II).

3.4 铝

如前所述, 铝并非重金属, 也非营养元素. 铝主要由大气尘埃带入海洋, 且在表层水中的停留时间很短, 故可作为尘埃从陆地到表层海洋的示踪剂^[8]. 在 GEOTRACES 计划中, 铝被明确指定为进入海洋的限制性营养元素铁的示踪物^[152]. 适用于海水中铝的现场检测方法很少, 主要原因是海水基体复杂, 溶解态铝的浓度极低, 准确测定有较大难度. 2007 年, Tira 等^[8]对天然水中铝的测定技术进行了综述, 重点介绍了船载海水分析方法, 包括采样、过滤、存储和测定等.

络合衍生-分光光度法是测定淡水中铝的常用方法, 铬天菁 S 分光光度法被列为我国生活饮用水

检测铝的标准方法^[153], 但其灵敏度低、干扰离子多、pH 反应条件苛刻, 极少用于海水分析. 仅有 Zhou 等^[154]结合 IDA 的分离富集技术, 采用 FA-SPE (IDA)-铬天菁 S 分光光度法, 在九龙江河口走航测定痕量铝, 检出限和测定上限分别为 $0.80 \text{ nmol} \cdot \text{L}^{-1}$ 和 $250 \text{ nmol} \cdot \text{L}^{-1}$, 通过减少富集体积还可提高测定上限.

可与铝生成荧光物质的络合试剂有荧光镓、水杨醛、桑色素、铬变酸等, 但大多数荧光法仅用于地表水中铝的测定. 海水中痕量铝的现场分析方法大多以荧光镓荧光光度法为基础, 结合 FA 技术和 SPE 等分离技术而建立. 1994 年, Resing 等^[155]首次以改性 8-HQ 树脂富集痕量铝, 结合 FIA 和 LMG 荧光光度法, 现场测定了太平洋某剖面中的痕量铝, 检出限达 $0.15 \text{ nmol} \cdot \text{L}^{-1}$. 此后, Brown 等^[156]对此方法进行改进, 采用商品 IDA 树脂取代自行制备的改性 8-HQ 树脂, 建立了 FA-SPE (IDA)-荧光镓荧光光度法, 在保证方法检出限 ($0.1 \text{ nmol} \cdot \text{L}^{-1}$) 的同时提高了重现性. Suárez 等^[157]基于注射泵, 以分散液-液微萃取-荧光镓荧光光度法, 测定近岸海水中的铝, 检出限达 $\text{nmol} \cdot \text{L}^{-1}$ 级别. Spolaor 等^[126]采用荧光镓荧光光度法, 测定了冰芯中的铝 (检出限 $0.13 \text{ ng} \cdot \text{g}^{-1}$). Kara 等^[158, 159]采用 *N*-*o*-香草醛-2-氨基-*p*-甲酚作为络合-荧光试剂, 结合 FA 技术测定天然水包括海水中的铝, 检出限为 $2.1 \text{ nmol} \cdot \text{L}^{-1}$.

4 现存问题与展望

(1) 随着海洋研究对数据数量和质量要求的日益提高, 海水中痕量营养盐和金属的分析方法研究也逐步深入. 欲从高盐基底中检出痕量目标物, 分析方法必须具备高灵敏度、强抗干扰能力. 总体而言, 当前现场和原位的检测方法仍然以分子光谱法为主, 成熟的仪器也大多基于分子光谱法. 分子光谱法的紫外-可见分光光度法、荧光光谱法和化学发光法各有千秋; 紫外-可见分光光度法的抗干扰能力较强但灵敏度较差, 荧光光谱法和化学发光法的灵敏度较高但受环境因素和其他化合物的干扰较大.

(2) 利用催化反应可在一定程度上提高分光光度法的灵敏度; 结合 FA 的流路设计, 利用密闭管道及在线小柱预富集, 可较好地提升分子光谱检测对恶劣环境的适应性和抗海水基底干扰的能力, 提高重现性, 降低检出限. 通过增加吸收光程长度提高灵敏度, 已经在 LWCC 的应用中得到极佳的体现. 因此, 关注有机合成领域和材料学领域的最新进展, 探索新的反应机制, 制备新的反应试剂、富集吸附剂和光学材料, 是突破现有方法瓶颈的途径之一.

(3) 化学反应中所添加化学试剂的纯度, 将极大地影响试剂空白进而影响方法检出限. 不同厂家、不同批次的化学试剂含有的杂质可能不同, 或导致实验结果不能重现. 试剂的提存已经为科学家所重视. 在 FA 系统中在线生成和在线净化试剂, 值得关注 and 尝试. 另外, 尽量少使用化学试剂, 尽量采用直接检测手段, 并非仅是为了降低试剂空白, 更是为了实现原位长期观测.

(4) 虽然上述的海水化学分析主要涉及化学问题, 但检测器的性能亦不容忽视. 对于海洋现场和原位仪器来说, 在改善分子光谱仪器的光源和光电元件, 进行电子降噪, 采用新的器件和技术, 提高加工和制造工艺等方面, 还有很大的提升空间. 从数理统计学和算法的角度对数据进行深度处理, 亦能提高信噪比, 提高精度和选择性.

(5) 在应用方面, 从岸基实验室到船基实验室; 从现场快速检测到原位长期观测; 从常量分析到痕量分析再到超痕量分析; 从河口到近岸再到深远海; 随着海洋环境科学家们探索空间的日益拓展, 自动化和智能化仪器的需求将持续增加. 研发适用于各种应用场合的 FA 衍生技术, 将越来越受到重视.

(6) 最后, 虽然本文没有专门讨论痕量分析的采样技术, 实际上, 即使在走航分析和原位分析中, 尤其对痕量金属的测定而言, 水样如何进入测定系统、要不要过滤等, 均需要认真考虑. 如果是采样后回到实验室再行分析, 更是要面对样品如何采集分装、是否和如何添加保护剂、怎样控制储存时间和运输条件等一系列问题. 这些细节均涉及数据的准确性, 也是需要认真解决的.

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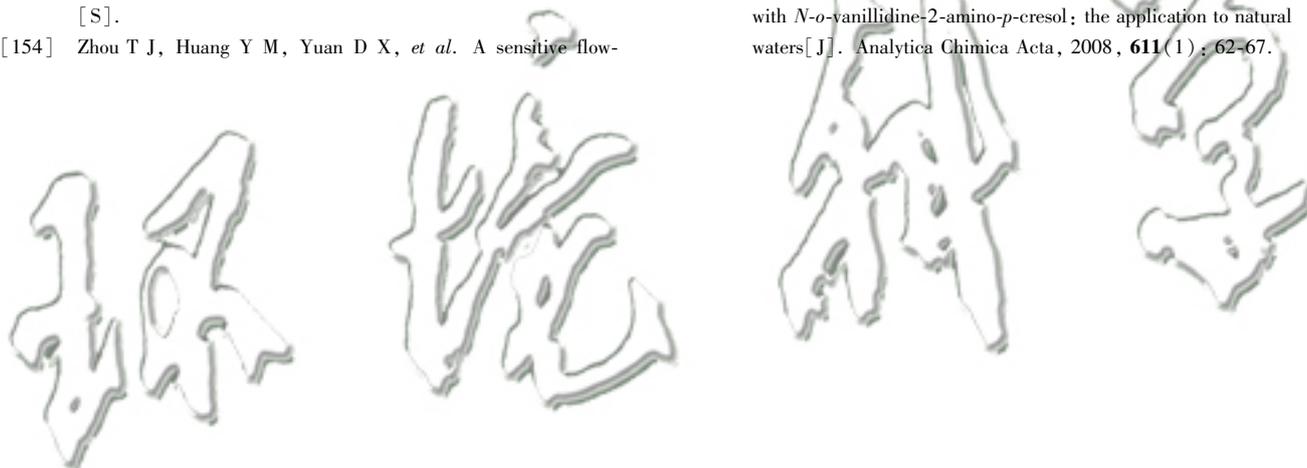
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