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两种水体铜配合容量测试方法的适用性比较及应用

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摘要: 配合(络合)容量是影响重金属在水体中环境行为的重要指标. 为比较两种测量方法测量值的差异及人为污染物对配合容量的影响, 以乙二胺四乙酸(EDTA)和安赛蜜分别作为强、弱配体, 对水体铜配合容量(CuCC)的双硫脲萃取动力学测试法(萃取法)和离子选择电极测试法(电极法)进行验证和比较. 研究发现, 萃取法更适合用于测定水体中强配体对CuCC的贡献, 而电极法的测试结果与水溶液中强、弱配体的存在均有关联. 两种方法对实际水体的测定结果显示, 电极法对水库、排污河等地表水体CuCC的测定值($86.9 \sim 227.0 \mu\text{mol} \cdot \text{L}^{-1}$)比萃取法($9.9 \sim 14.6 \mu\text{mol} \cdot \text{L}^{-1}$)高约1个数量级, 而对于垃圾渗沥液, 电极法的测定值($6\,998.4 \sim 31\,005.8 \mu\text{mol} \cdot \text{L}^{-1}$)比萃取法($89.6 \sim 109.1 \mu\text{mol} \cdot \text{L}^{-1}$)高2个数量级. 结果表明, 污染受纳水体重金属络合容量的升高主要是由弱配体化合物增加导致, 且弱配体的含量与水体氨氮和有机氮的总和具有显著的相关性($R=0.975$, $P<0.01$).

关键词: 配合容量; 天然水体; 铜; 萃取动力学法; 离子选择电极法

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Applicability Comparison and Application Study of Two Methods for Determination of the Copper Complexing Capacity of Waters

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Abstract: Complexing capacity (CC) is an important indicator affecting the environmental behavior of heavy metals in water, which can be determined by different methods based on different mechanisms. To validate and compare the applicability of different methods in CC determination, the complexing capacity of Cu^{2+} (CuCC) in solutions of ethylenediamine tetraacetic acid (EDTA) and acesulfame was determined by methods of dithizone extraction kinetics (DEK) and ion-selective electrodes (ISE), while EDTA and acesulfame were selected to represent strong and weak ligands in water, respectively. DEK method was found to be more suitable for determining the contribution of strong ligands to CuCC, while the results determined by ISE were related to both the strong and weak ligands in water. DEK and ISE methods were used to measure CuCC of several actual water samples, including samples from reservoir, discharge river, fishpond, and landfill leachates. CuCC in the water samples of the reservoir and discharge river measured by ISE were $86.9 \sim 227.0 \mu\text{mol} \cdot \text{L}^{-1}$, which were about one order of magnitude higher than those measured by DEK ($9.9 \sim 14.6 \mu\text{mol} \cdot \text{L}^{-1}$). For the landfill leachates, CuCC measured by ISE were $6\,998.4 \sim 31\,005.8 \mu\text{mol} \cdot \text{L}^{-1}$, which were 2 orders of magnitude higher than those by DEK ($89.6 \sim 109.1 \mu\text{mol} \cdot \text{L}^{-1}$). The increase of CuCC in the polluted water samples might be due to the weak ligands like pollutants. A positive correlation ($R=0.975$, $P<0.01$) was found between the CuCC related to the weak ligands (ΔCuCC) and the sum concentration of ammonia nitrogen and organic nitrogen in waters.

Key words: complexing capacity; natural waters; copper; the extraction kinetics method; the ion-selective electrodes method

在水环境中, 重金属的形态分布影响着重金属的毒性和生物可利用性. 水体中存在的天然来源配体, 如碳酸根、硫酸根、磷酸根等无机阴离子, 以及腐殖酸、富里酸等大分子有机物, 都可能与水中的游离态重金属阳离子形成配合物. 此外, 一些人为排放的有机污染物也被发现可与重金属发生配合反应^[1-4]. 为评价水体对金属离子的配合能力, 配合(络合)容量(complexing capacity, CC), 即天然水体中能与金属产生配合的配体总量这一指标被提

出^[5-7]. 基于不同原理, 测试水体配合容量的不同方法, 如伏安法、螯合树脂法、溶剂萃取法和离子选择电极法等, 被逐渐建立^[8-11]. 其中, 双硫脲萃取法作为一种基于动力学理论的分析方法, 由于可同

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时测试金属离子络合容量和金属配合物的易变性常数,因此被一些研究者采用^[12]。而离子选择电极法由于可以直接测出溶液中金属离子活度且操作简便,也被作为是测试金属离子络合容量的常用方法^[11]。然而,仅有的少量比较研究表明^[12],不同测试方法对水体重金属配合容量的测试结果可能存在较大差异。并且对于不同测试方法适用性的比较研究并不多见。此外,尽管人为排放的污染物中可能含有多种重金属的配体化合物,但相比于腐殖质类天然有机配体,人为污染排放对水体配合容量的贡献还尚待评估。

有机螯合剂乙二胺四乙酸(EDTA)和人工甜味素安赛蜜是水体中常见的污染物。EDTA向自然环境的年释放量估计值高达25 000 t^[13]。而作为最重要的人工甜味剂,安赛蜜在污水处理厂出水及地表水中的浓度可高达46 $\mu\text{g}\cdot\text{L}^{-1}$ ^[14]和>2 $\mu\text{g}\cdot\text{L}^{-1}$ ^[15];同时,安赛蜜与重金属在溶液中的配合行为也已被证实^[16]。本研究以乙二胺四乙酸和安赛蜜分别代表铜离子的强配体和弱配体化合物,对应用双硫脲萃取动力学法和离子选择电极法测试配体化合物水溶液铜配合容量(CuCC)的效果进行比较。在此基础上,采用上述方法测试实际水体的CuCC,初步探讨人为排放污染物对天然水体配合容量的潜在贡献。水体重金属配合容量作为评价重金属水环境行为的重要指标,在重金属环境风险评估领域具有应用潜力;本文对该指标不同测试方法适用性的比较研究,有利于深入理解水体配合容量概念的内涵,以期这一指标在环境风险评估领域的应用提供依据。

1 材料方法

1.1 试剂和仪器

EDTA、双硫脲、氯仿、硝酸铜 $[\text{Cu}(\text{NO}_3)_2]$ 为分析纯;硝酸钾(KNO_3)与氢氧化钠(NaOH)为优级纯;安赛蜜标准品(99%);硝酸($\geq 65\%$)。使用超纯水进行试剂配制。

测试使用实际水样包括采自天津某水库不同位置的水样(即水库水1、2、3)、相邻区域的鱼塘水样(鱼塘水),附近某排污河水样(排污河水),以及2个垃圾填埋场的渗沥液样品(渗沥液A、B)。水样经0.45 μm 滤膜过滤,测试前根据需要稀释不同倍数。

电感耦合等离子体质谱(ICP-MS)(珀金埃尔默Elan DRC-e);pH计(雷磁pHS-3C),铜离子选择电

极(雷磁PCu-1-01),参比电极[雷磁C(K_2SO_4)-1];水样成分分析仪(Aanalytik Jena multi N/C 3100);电导仪(雷磁DDS-307)。

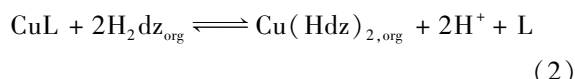
1.2 双硫脲萃取动力学法测水体Cu的配合容量

1.2.1 试验原理

当水样中加入过量 Cu^{2+} 后,水中配体(L)与 Cu^{2+} 发生配合反应^[17]:



当以双硫脲(H_2dz)为水相中配体的竞争配体,以双硫脲的氯仿溶液作为有机相(org)对水样进行萃取时,可发生如下反应^[10]:



用准一级反应动力学描述反应,可积分得到公式如下:

$$\ln[\text{CuL}]_t = \ln(\text{CuL})_{t=0} - kt \quad (3)$$

式中, $[\text{CuL}]_t$ 为不同时间 t 测定水相中总 Cu^{2+} 浓度, k 为配合物的易变常数^[18]。将 $\ln[\text{CuL}]_t$ 和 t 进行线性拟合,所得 $[\text{CuL}]_{t=0}$ 即为CuCC。

1.2.2 试验步骤

萃取试验参照文献[10, 18, 19]描述的过程进行。采用双硫脲的氯仿溶液对含 Cu^{2+} 浓度为 $2.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ 的水样进行液液萃取(Cu^{2+} 相对于配体过量)。在不同时间 t (10、20、30、40、50、60、80、120、160 s)移取上层水相溶液,用ICP-MS测试Cu浓度,即式(3)中 $[\text{CuL}]_t$ 。依公式(3)可拟合得到CuCC。

1.3 离子选择电极测水体Cu的配合容量

1.3.1 试验原理

配体L与 Cu^{2+} 发生配合反应的条件稳定常数 K 可定义如下:

$$K = \frac{[\text{CuL}]}{[\text{Cu}][\text{L}]} \quad (4)$$

由物质平衡可知:

$$[\text{Cu}]_t = [\text{Cu}] + [\text{CuL}] \quad (5)$$

$$[\text{L}]_t = [\text{L}] + [\text{CuL}] \quad (6)$$

式中, $[\text{Cu}]_t$ 为加入水样的总 Cu^{2+} 浓度, $[\text{Cu}]$ 为溶液中自由态 Cu^{2+} 浓度, $[\text{CuL}]$ 为溶液中配合态铜浓度, $[\text{L}]$ 为自由配体浓度, $[\text{L}]_t$ 为溶液中配体总浓度。合并公式(4)、(5)、(6),即得到Van den Berg方程^[20]如下:

$$\frac{[\text{Cu}]}{[\text{Cu}]_t - [\text{Cu}]} = \frac{[\text{Cu}]}{[\text{L}]_t} + \frac{1}{K[\text{L}]_t} \quad (7)$$

通过离子选择电极测定溶液中自由态 Cu^{2+} 浓

度 $[\text{Cu}]$, 并计算加入的总 Cu^{2+} 浓度 $[\text{Cu}]_t$, 将 $\frac{[\text{Cu}]}{[\text{Cu}]_t - [\text{Cu}]}$ 和 $[\text{Cu}]$ 进行线性拟合, 根据直线斜率和截距即可求出 $[\text{L}]_t$ 和条件稳定常数 K , $[\text{L}]_t$ 即等于水体的 CuCC .

1.3.2 试验步骤

根据离子选择电极使用要求, 配制不同浓度 $\text{Cu}(\text{NO}_3)_2$ 标准溶液, 绘制电压值和离子浓度负对数值的标准曲线. 水样中加入 KNO_3 , 使其浓度为 $0.10 \text{ mol} \cdot \text{L}^{-1}$ (调节离子强度), 使用 NaOH 和 HNO_3 稀溶液调节水样 pH 至 7.0 ± 0.1 . 向样品中逐滴加入 $\text{Cu}(\text{NO}_3)_2$ 溶液, 加入过程中温度保持在 $25^\circ\text{C} \pm 1^\circ\text{C}$, 记录滴入水样中的 Cu^{2+} 总量, 并计算 $[\text{Cu}]_t$, 同时记录滴入过程中溶液的电压值变化, 根据电压值求得水样中自由态 Cu^{2+} 浓度 $[\text{Cu}]$, 当溶液中自由 Cu^{2+} 浓度达到 $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ 时结束滴定. 然后根据式(7)计算 CuCC .

1.4 水质参数测试

水样的总有机碳 (TOC)、无机碳 (IC)、总碳 (TC) 和总氮 (TN) 采用 Analytik Jena multi N/C 3100 仪器测试, 电导率值采用雷磁 DDS-307 测试. 水体中氨氮 ($\text{NH}_4^+ - \text{N}$) 采用纳氏试剂法 (GB/T 7479-87) 测定, 硝酸盐氮和亚硝酸盐氮的检测分别采用紫外分光光度法 (HJ/T 346-2007) 和 N -(1-萘基)-乙二胺分光光度法 (GB/T 7493-87) 进行, 有机氮 (TON) 含量由 TN 与各主要无机氮浓度的差值计算获得.

2 结果与讨论

2.1 双硫腙萃取动力学法对模拟配体水溶液配合容量的测试

对不加入任何配体的空白水样进行的萃取试验表明, 在 10 s 内水样中的自由态 Cu^{2+} 可被完全萃取. 因此在使用萃取法过程中使用 10 s 后的数据点进行拟合. 使用双硫腙萃取动力学法对 EDTA 水溶液 ($5.0 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$) 的 CuCC 进行测定中发现, 在 10 ~ 60 s 内水中 Cu^{2+} 剩余浓度随时间减少 (图 1), 这一过程可用准一级动力学方程 [式(3)] 描述. 拟合结果表明, EDTA 水溶液的 CuCC 为 $5.86 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$ ($R=0.99, P<0.001$). CuCC 与 EDTA 浓度的比值为 1.17, 说明萃取法测得的溶液 CuCC 与 EDTA 这一强配体浓度较为吻合. 有研究者验证双硫腙萃取法对已知浓度的次氨基三乙酸 (NTA) 溶液铜络合容量测试的适用性时^[10], 也取得了与本研究类似的结果.

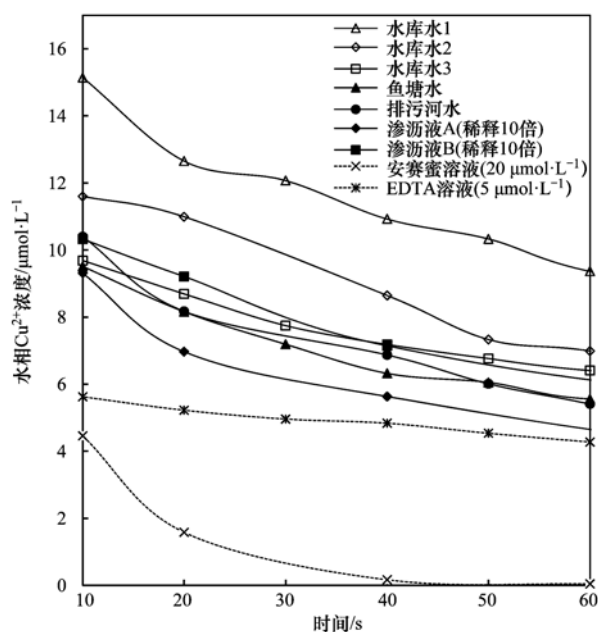


图1 双硫腙萃取不同水样过程中水相中 Cu^{2+} 浓度随时间变化曲线

Fig. 1 Changes of Cu^{2+} concentration in aqueous phase as a function of extraction time in the dithizone extraction process for different water samples

相比于 EDTA, 安赛蜜分子对金属离子的配合能力较弱^[21, 22], 与双硫腙竞争 Cu^{2+} 的能力较差. 因此, 在安赛蜜溶液 ($20 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$) 的 CuCC 测试中, Cu^{2+} 在 40 s 内即全部被从水相中萃取. 由于反应迅速, 难以取得足够多的可准确反映水相 Cu^{2+} 浓度变化的数据点, 因而无法得到可信的拟合结果. 可见, 应用萃取动力学法难以测定弱配体化合物对水体配合容量的贡献.

2.2 铜离子选择电极法方法验证

在 EDTA 水溶液 ($5.0 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$) 和安赛蜜水溶液 ($20 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$) 中逐渐加入 Cu^{2+} , 可引起溶液中自由 Cu^{2+} 浓度的不同变化 (图 2). 根据本试验所使用铜离子选择电极的测定范围, 选择 Cu^{2+} 浓度测定值在 $1 \times 10^{-6} \sim 1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ 范围内的数据点进行回归分析.

使用电极法对上述溶液 CuCC 的测试表明, Cu^{2+} 不断加入过程中, 水中 Cu^{2+} 浓度的变化符合 Van den Berg 方程 ($R>0.95, P<0.01$). 对于强配体 EDTA, 加入模拟配体的量与实际测定值基本一致. 电极法测定 $5 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$ EDTA 溶液所得 CuCC ($5.04 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$) 与 EDTA 浓度的比值约为 1.01, 且该结果与萃取法测得的 CuCC 近似. 相比之下, $20 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$ 安赛蜜溶液的 CuCC 测量值仅为 ($2.02 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$), 与安赛蜜摩尔浓度的比值约为 0.10.

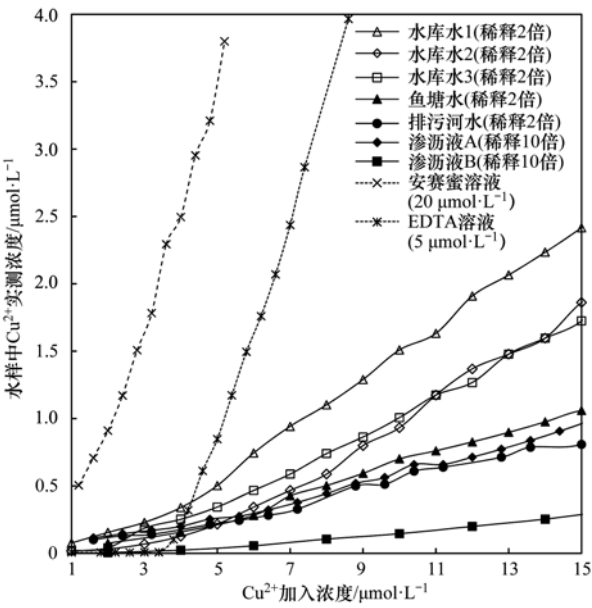


图2 离子选择电极法测定不同水样中自由态 Cu^{2+} 浓度变化曲线

Fig. 2 Changes of free Cu^{2+} concentration in different water samples detected by the ion-selective electrodes method

这印证了安赛蜜与 Cu^{2+} 配合能力较弱,在此试验条件下仅有 10% 的分子与 Cu^{2+} 形成配合物.

2.3 两种方法对实际水样配合容量的测试结果比较

使用萃取法对地表水体的 CuCC 的测试结果 (表 1) 表明,实际水样中所加入 Cu^{2+} 的萃取动力学均可用准一级动力学方程描述 ($R > 0.95$, $P < 0.05$). 对于水库水、鱼塘水和排污河水样,萃取法测得的 CuCC 变化范围在 $9.9 \sim 14.6 \mu\text{mol}\cdot\text{L}^{-1}$. 与预计结果不同,萃取法测得的排污河水样 CuCC 并未显著高于其他水样. 这可能意味着该排污河污水中,可作为铜的强配体的污染物存在水平较低,因此对萃取法的 CuCC 测量值贡献较小. 与上述水样相比,萃取法测得垃圾渗沥液中 CuCC 的数值更大 ($89.6 \sim 109.1 \mu\text{mol}\cdot\text{L}^{-1}$),表明渗沥液中存在较大数量强配体型污染物. 之前有研究发现,垃圾渗沥液中溶解性有机物 (DOM) 不同组分中,类富里酸和类蛋白组分与重金属具有较强的配合能力^[23]. 由易变形常数 k 值可以看出,天然水样和排污河水样的配合物的平均稳定性小于 EDTA 铜配合物 ($k = 0.52 \times 10^{-2} \text{ s}^{-1}$) 的稳定性.

电极法对地表水体及垃圾渗沥液的 CuCC 测试结果表明 (表 2),地表水体中 CuCC 测量值范围在 $86.9 \sim 227.9 \mu\text{mol}\cdot\text{L}^{-1}$,比萃取法测量值高约 1 个数量级. 与萃取法所得结果不同,鱼塘和排污河水中 CuCC 的电极法测量值比水库水高 1 倍. 而在垃

圾渗沥液中观察到更高水平的 CuCC 电极法测量值,分别高达 $31\,005.8 \mu\text{mol}\cdot\text{L}^{-1}$ 和 $6\,998.4 \mu\text{mol}\cdot\text{L}^{-1}$. 上述结果表明,水体中人为排放的污染物,可能导致水体中弱配体的显著增加. 尽管鱼塘从临近水库不定期取水,但鱼塘水的 CuCC 明显高于水库水,这可能与鱼塘中的饲料投加和鱼类排泄物有关. 已有研究发现,鸡粪 DOM 相比于土壤 DOM,呈现出更大的金属配合能力^[24].

表 1 双硫腙萃取动力学法对水样中铜配合容量的测定结果¹⁾

Table 1 CuCC of water samples determined by the dithizone extraction kinetics method

水样	CuCC/ $\mu\text{mol}\cdot\text{L}^{-1}$	$k \times 10^{-2}/\text{s}^{-1}$	R	P
水库水 1	14.6	0.71	0.985	$<1 \times 10^{-4}$
水库水 2	11.8	0.79	0.983	$<1 \times 10^{-4}$
水库水 3	9.9	0.83	0.976	$<1 \times 10^{-4}$
鱼塘水	10.2	1.06	0.985	$<1 \times 10^{-4}$
排污河水	11.2	1.23	0.987	$<1 \times 10^{-4}$
渗沥液 A	109.1	0.88	0.954	0.012
渗沥液 B	89.6	0.98	0.979	0.001

1) k : 易变形常数

表 2 离子选择电极法对水样铜配合容量的测定结果¹⁾

Table 2 CuCC of water samples determined by the ion-selective electrodes method

水样	CuCC/ $\mu\text{mol}\cdot\text{L}^{-1}$	$\lg K$	R	P
水库水 1	103.2	5.12	0.986	$<1 \times 10^{-4}$
水库水 2	86.9	5.38	0.992	$<1 \times 10^{-4}$
水库水 3	98.6	5.32	0.972	$<1 \times 10^{-4}$
鱼塘水	227.9	5.15	0.997	$<1 \times 10^{-4}$
排污河水	213.6	5.23	0.995	$<1 \times 10^{-4}$
渗沥液 A	31 005.8	5.17	0.994	$<1 \times 10^{-4}$
渗沥液 B	6 998.4	5.41	0.988	$<1 \times 10^{-4}$

1) K : 条件稳定常数

水样 CuCC 的电极法测量值均高于萃取法测量值,这是由于离子选择电极可以直接测得游离的 Cu^{2+} 活度,因而在测定 CuCC 过程中可反映所有已与 Cu^{2+} 发生配合的配体总量^[25];而双硫腙萃取法测定的 CuCC 仅包括可与双硫腙竞争铜离子的稳定有机、无机配合物和胶体^[18, 26].

2.4 配合容量与水质指标相关性分析

将水样和渗沥液中 TOC、IC、TC、TN、电导率值等水质指标与水样 CuCC 的萃取法测量值 ($\text{CuCC}_{\text{extr}}$)、电极法测量值 ($\text{CuCC}_{\text{elec}}$) 以及二者的差值 ΔCuCC 分别进行线性相关性分析,结果表明 TOC、IC、电导率等与上述配合容量测量值均无显著相关关系. 然而, ΔCuCC 被发现与水样的 TN 具有较显著的相关性 ($R = 0.949$, $P < 0.05$) (图 3), ΔCuCC 可视为反映水体中弱配体 (不稳定的有机和无机络

合物,不稳定的有机和无机胶体)对 CuCC 的贡献,该结果意味着,水体中存在的氨氮与含氮有机物,可能是水环境中铜的弱配体重要来源. 对于铜氨配合物的形成和应用,目前已有较多认知. 而 Seo 等^[27]在研究垃圾渗沥液 DOM 与铜离子的配合反应过程时也发现,芳香族氨基酸类荧光基团是铜离子的重要配体. 此外,部分含氮杂环化合物与铜离子之间的较强配合反应目前也有较多报道^[28].

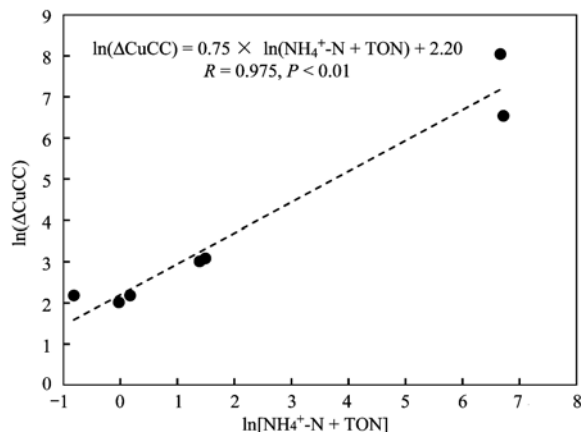


图3 ΔCuCC 与水体氨氮和总有机氮浓度之和 ($[\text{NH}_4^+-\text{N} + \text{TON}]$) 的相关关系

Fig. 3 Correlation between ΔCuCC and $\text{NH}_4^+-\text{N} + \text{TON}$ in water sample

3 结论

萃取动力学法和离子选择电极法均可用于水体中 CuCC 的测定. 萃取法的测量结果可反映水体中强配体的存在水平,而电极法的测量结果则反映了强弱配体对 CuCC 的综合贡献. 通过两种方法的 CuCC 测量值比较发现,人为排放的污染物可导致本研究涉及实际水体中的弱配体数量的显著增加. 含氮有机物和氨氮与水样中弱配体化合物的存在水平成正相关. 尽管上述两种方法均可用于水体的重金属配合容量测定,但不同方法所得的测量值对于评估重金属污染物迁移及生物富集行为的意义,尚需进一步研究.

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