



# Organic complexation and total dissolved trace metal analysis in estuarine waters: comparison of solvent-extraction graphite furnace atomic absorption spectrometric and chelating resin flow injection inductively coupled plasma-mass spectrometric analysis

Kuria Ndung'u<sup>a,\*</sup>, Robert P. Franks<sup>a</sup>, Kenneth W. Bruland<sup>b</sup>, A. Russell Flegal<sup>c</sup>

<sup>a</sup> *Institute of Marine Sciences, University of California at Santa Cruz, Santa Cruz, CA 95064, USA*

<sup>b</sup> *Department of Ocean Sciences, University of California at Santa Cruz, Santa Cruz, CA 95064, USA*

<sup>c</sup> *Department of Environmental Toxicology, University of California at Santa Cruz, Santa Cruz, CA 95064, USA*

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## Abstract

The measured concentrations of cadmium, cobalt, copper, nickel, lead, zinc, and manganese in acidified ( $\text{pH} < 2$ ) estuarine water samples analyzed for total dissolved trace metal concentrations using on-line chelating resin column partitioning with inductively coupled plasma-mass spectrometry (CRCP-ICP-MS) were compared to those analyzed by graphite furnace atomic absorption spectrometry (GFAAS) after liquid–liquid extraction using a combination of 1-pyrrolidinedithiocarbamate/diethyldithiocarbamate (PDC/DDC). Although there was good agreement between the two sets of analyses for cadmium, lead, manganese, and zinc concentrations, those of cobalt, copper, and nickel determined by CRCP-ICP-MS were found to be 10–20% lower than those determined by solvent-extraction GFAAS. The different yields were positively correlated ( $R > 0.961$ , simple linear regression) to the dissolved organic carbon (DOC) concentration of the samples. Good agreement between the two methods for cobalt and copper was achieved after ultraviolet (UV) digestion of the acidified samples. Samples collected from the South Bay of the San Francisco Estuary with high DOC showed the greatest difference for cobalt, copper, and nickel which is tentatively attributed to complexation with humic material for copper and cobalt and strong synthetic chelating agents such as ethylenediaminetetraacetic acid (EDTA) for nickel. This is consistent with previous studies on copper, nickel and cobalt complexation in this region. We recommend UV digestion of acidified estuarine samples prior to multi-element analysis by chelating resin flow injection ICP-MS methods.

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## 1. Introduction

Studies undertaken during the last two decades have shown that organic complexation is impor-

tant for a number of trace metals in estuarine and seawater. An important fraction (30–99.9%) of metals, including cobalt [1–3], copper [4–6] iron [7,8], nickel [4,9], and zinc [10–12], are complexed by natural and anthropogenic organic ligands in estuarine and seawater. This organic complexation is thought to decrease metal reactivity and scavenging by suspended particulate matter, thereby maintaining

\* Corresponding author. Tel.: +1-831-459-4098;

fax: +1-831-459-3524.

E-mail address: [kndungu@es.ucsc.edu](mailto:kndungu@es.ucsc.edu) (K. Ndung'u).

enhanced dissolved trace metal concentrations in seawater.

The metal–organic ligand complexes are strong, with reported conditional stability constants ( $\log K_{\text{MeL}}^{\text{cond}}$ ; where  $\text{Me}^{n+}$  is the metal and L the ligand) for Co(II) (15.6–16.1) [2,3], Cu(II) (10–13) [5], Fe(III) (18.8–21.2) [11], Ni(II) (>17) [4], and Zn(II) (10) [12,13]. In order to determine total dissolved trace metal concentrations when using a preconcentration step such as chelating resin column partitioning, it is necessary to release the trace metal from the metal–organic complex prior to analysis. Furthermore, the removal of dissolved organic matter (DOM) from samples is also preferable, as some DOM may re-complex with the trace metals prior to partitioning onto the chelating resin.

The nature of DOM in estuarine and seawater is complex, but is thought to include humic acids, fulvic acids, glycollic acid, peptides, proteins, amino acids, lipids and polysaccharides. In coastal waters and estuaries, DOM may also include anthropogenic chelating ligands such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetate (NTA), phosphonates, citric acid, tartaric acid and surfactants from anthropogenic sources [6,10,14].

Since the high concentration of alkali and alkaline earth metal ions in seawater (ca. 500 and 60 mM, respectively) makes direct analysis of seawater even by the most sensitive analytical techniques such as ICP-MS very difficult, a separation and preconcentration step to separate the trace metals of interest from these major ions is necessary. Solvent-extraction and chelating resin column partitioning (CRCP) are two of the most common sample concentration methods used for this purpose. One of the most common solvent-extraction methods uses a combination of 1-pyrrolidinedithiocarbamate and diethyldithiocarbamate (PDC/DDC) to simultaneously concentrate the trace metals and remove the salt matrix interference [15,16]. This method has been proven to be reliable and is widely used for the extraction of trace metals from sea and estuarine water prior to analysis by graphite furnace atomic absorption spectrometry (GFAAS) or inductively coupled plasma-mass spectrometry (ICP-MS) [17–19]. However, the PDC/DDC solvent-extraction method although very reliable, is time consuming and difficult to automate because it is not readily adapted to flow injection systems. Wells

and Bruland [20] developed a solid phase extraction method employing a more water soluble form of the dithiocarbamate ligand (dihydroxyethyldithiocarbamate) in a flow system where the dithiocarbamate first formed complexes with the metals of interest and then isolated these complexes on a C-18 resin.

Iminodiacetate-based chelating resins such as Chelex-100 or immobilized ligands such as 8-hydroxyquinoline possess high selectivity for transition metal ions with minimal retention of alkali and alkaline earth metal ions. These resins can easily be packed in mini columns, which allows the preconcentration/separation step to be incorporated in a flow system. While a major drawback on the use of Chelex-100 resin in flow injection systems is its swelling characteristic, other iminodiacetate resins with higher cross-linking (e.g. Metpac<sup>®</sup> or Toyo-Pearl<sup>®</sup>) are not prone to swelling. This makes automation of the set-up easier and allows easy on-line connection to flow-through detectors [21,22] or more recently to ICP-MS [23–27].

Although iminodiacetate-based chelating resins extract free metal ions and kinetically labile forms, they do not necessarily isolate those metals when strongly complexed by organic ligands. Since acidified samples must have their pH adjusted up prior to the CRCP step, some of the metal can re-complex and become bound as kinetically inert complexes with organic ligands that can pass through the column. Such organic complexation may cause the trace metals to be non-reactive (non-labile) with respect to the CRCP step unless the DOM is destroyed.

A preferred approach for the breakdown of dissolved metal–organic complexes and the removal of DOM involves treatment of the sample with ultraviolet (UV) radiation prior to trace metal determination [9,12,28]. UV digestion is a trace metal clean sample pretreatment method, as it does not require the addition of large amounts of oxidants. Furthermore, UV digestion is effective and can be readily incorporated in flow injection manifolds, allowing stand-alone trace metal analysis [29–31].

Consequently, UV irradiation has been used to break down organic matter in estuarine water samples prior to voltammetric or chemiluminescence determination. For example, Whitworth et al. [31] used an on-line UV digestion system for on-line determination of nickel in Tamar estuary (Great Britain). More

recently, Achterberg et al. [9] carried out a study on the effectiveness of batch and on-line UV digestion of estuarine and seawater samples prior to copper determination using flow injection with chemiluminescence detection.

There has been an increase in the use of CRCP methods for trace metal preconcentration/separation prior to on-line or off-line analysis in the last few years. However, very few studies have investigated the effect of organic complexation on the performance of CRCP for the determination of total dissolved trace metals in estuarine waters. Such studies are important because most of these methods involve on-line pH adjustment (to  $\text{pH} > 5$ ) of the acidified samples prior to CRCP extraction. There is, therefore, an inherent risk of the trace metals re-complexing with the dissolved organic ligands at the higher pH to form non-labile complexes prior to CRCP binding.

Mackey et al. [32] reported reduced extraction recovery of cadmium, cobalt, copper and nickel from unfiltered Derwent estuary (Australia) water samples compared to Milli-Q<sup>®</sup> water metal standards using the PDC/DDC solvent-extraction technique. Although the authors did not identify the reason for the lower extraction efficiency in those unfiltered samples, they noted that it was strongly correlated to the presence of high concentrations of suspended solids and dissolved organic matter. Gueguen et al. [33] also noted that UV irradiation was necessary to destroy organic complexation of cadmium, copper and lead from a humic acid reference solution and spiked natural water solutions prior to CRCP-ICP-MS determination. Recently, Beck et al. [23] reported an automated CRCP-ICP-MS method for the determination of cadmium, copper, manganese, nickel, and zinc, in estuarine waters. That study compared the concentrations of cadmium, copper, nickel and zinc, measured using the PDC/DDC solvent-extraction procedure and manganese measured using differential pulse cathodic stripping voltammetry (DPCSV) with the on-line CRCP-ICP-MS method. The effect of organic complexation, however, was not realized in that study because only two samples were compared.

This paper, therefore, presents results of a more detailed study on the effect of organic complexation on the on-line CRCP-ICP-MS analysis of estuarine water samples from the San Francisco Bay Estuary (SFBE). We investigated the effectiveness of batch UV diges-

tion on SFBE water samples representing a wide spatial variability in dissolved organic carbon (DOC) and salinity. The samples included relatively fresh waters from the estuary in the North Bay which are strongly influenced by the Sacramento and San Joaquin rivers, as well as from the South Bay, which has a high anthropogenic DOC input from the surrounding industrial and residential sources.

## 2. Experimental

### 2.1. Reagents

All solutions were prepared with de-ionized water ( $18 \text{ M}\Omega \text{ cm}^{-1}$ ) from a Milli-Q<sup>®</sup> analytical reagent-grade water purification system (Millipore, Bedford, MA).  $\text{HNO}_3$  (Optima grade, Fisher Scientific, Pittsburgh, PA) was diluted with Milli-Q<sup>®</sup> to make up 1.5 M  $\text{HNO}_3$  eluent, and then spiked with  $10 \mu\text{g l}^{-1}$  each of  $^{103}\text{Rh}$  and  $^{69}\text{Ga}$  to be used as an internal standard. Acetic acid/ammonia buffer solution was prepared by slow addition of 15 ml of aqueous ammonia (20–22%, Optima grade, Fisher Scientific) to 13 ml of glacial acetic acid (trace metal grade, Fisher Scientific), diluted to 500 ml in an acid cleaned polyethylene bottle. The pH was adjusted to pH 5.0 with ammonia or acetic acid. A pH 5.0 wash solution was prepared by a 10-fold dilution of the above buffer and adjusted to pH 5.0 with  $\text{HNO}_3$ . The pH 9.0 buffer was similarly prepared by adding 18 ml of ammonia solution to 13 ml of glacial acetic acid and making up to 500 ml. For external calibration determination, multi-element working standard solutions were prepared by dilution of  $1000 \mu\text{g l}^{-1}$  stock solutions in 1.5 M  $\text{HNO}_3$ . The working standard solutions were acidified with hydrochloric acid to the same pH as the samples. The National Research Council of Canada certified estuarine water reference material SLEW-3, was used to assess the accuracy of the method.

### 2.2. Samples

The water samples used for these experiments were collected in May 1993 and in June and September of 1995 at 26 stations covering major geographical regions of the San Francisco Bay. The stations are located along a transect running from fresh waters at

the confluence of the Sacramento and San Joaquin rivers, through the Central Bay to the mouth of the Golden Gate and into the southernmost reaches of the South Bay. The sampling is part of the San Francisco Estuary Institute (SFEI) biannual-regional monitoring program for trace elements and other ancillary water quality parameters in San Francisco Bay [17,34]. The samples were acidified to pH 1.7–1.8 and stored acidified for at least a month prior to analysis. The samples were analyzed for cadmium, cobalt, copper, lead, nickel, and zinc. They were also analyzed for dissolved nutrients, chlorophyll-a and DOC. The trace metals were preconcentrated using the 1-pyrrolidinedithiocarbamate/diethyldithiocarbamate (PDC/DDC) solvent-extraction method [15]. Metal concentrations were measured by GFAAS using method of standard additions. Manganese concentrations were determined by cathodic stripping voltammetry [35,36]. Acidified aliquots of those samples were stored for seven to 9 years prior to analyses by CRCP-ICP-MS.

Samples from 12 out of the 26 sampling stations which were then chosen for the subsequent UV oxidation and CRCP-ICP-MS experiments were represen-

tative of the three main geographical regions of the estuary (Table 1).

### 2.3. UV oxidation experiments

The apparatus used for UV-digestion consisted of a medium pressure mercury discharge tube (1200 W; Hanovia, Union, NJ) positioned on the ceiling of a purpose-built aluminum housing (36 cm × 29 cm × 23 cm; UVO-cleaner model 342, Jelight Inc., Laguna Hills, CA) which was cooled by a fan. A digital photometer (model JL1400A, Jelight Inc., Irvine, CA) was used to monitor the power of the UV radiation during the oxidation. The average UV irradiation power was  $9.2 \pm 0.4 \text{ mW cm}^{-2}$  during the continuous operation of the Hg lamp. The housing was light tight to prevent exposure of personnel to harmful UV radiation and the power supply to the UV lamp was cut automatically upon opening the digestion unit. Medium pressure UV lamps produce ozone, and therefore, the aluminum housing is connected to an exhausting system. Experiments were carried out by placing up to three custom-made PTFE UV digestion cups (150 ml, 65 mm i.d.) fitted with quartz glass caps in the unit.

Table 1  
Sampling stations, DOC and salinity of the water samples from the San Francisco Bay Estuary used in this study

Code	Station	Latitude/longitude	Sampling date	Salinity	DOC (mg l <sup>-1</sup> )
BA05	San Jose	37°28'/121°58'	February 1995	5.0	5.525
BA30-s	Dumbarton Bridge	37°31'/122°08'	August 1995	22.2	3.003
BA30-w	Dumbarton Bridge	37°31'/122°08'	February 1995	16.5	3.315
BA40	Redwood Creek	37°33'/122°12'	February 1995	17.0	2.979
BB15	San Bruno Shoal	37°37'/122°17'	August 1995	24.2	2.174
BB70	Alameda	37°45'/122°19'	February 1995	14.7	2.871
BC10	Yerba Buena Island	37°49'/122°21'	August 1995	27.9	1.477
BC20	Golden Gate	37°45'/122°39'	February 1995	22.5	1.79
BC60	Red Rock	37°55'/122°26'	August 1995	25.1	1.489
BD20	San Pablo Bay	38°03'/122°25'	February 1995	11.7	2.462
BD50	Napa River	38°06'/122°16'	August 1995	14.3	2.258
BF20	Grizzly Bay	38°07'/112°02'	August 1995	5.5	1.982
BG20	Sacramento River	38°03'/121°48'	February 1995	0.0	2.486
BA20	South Bay	37°29'/122°05'	May 1993	21.5	2.847
BA30	Dumbarton Bridge	37°30'/122°07'	May 1993	22.2	2.799
BA40	Redwood Creek	37°33'/122°11'	May 1993	24.2	2.15
BB30	Oyster Point	37°40'/122°20'	May 1993	25.0	1.934
BC41	Point Isabel	37°53'/122°20'	May 1993	24.7	2.078
BD20	San Pablo Bay	38°03'/122°25'	May 1993	16.3	2.516
BF20	Grizzly Bay	38°06'/122°02'	May 1993	0.7	2.823
BG20	Sacramento River	38°04'/121°49'	May 1993	0.0	2.438

Table 2  
ICP-MS operating and acquisition parameters

Isotope	Mass window	Settling time (s)	Sample time (s)	Samples/peak	Segment duration (s)	Detection mode
Low resolution, 65 scans						
<sup>55</sup> Mn	5	0.050	0.010	100	0.050	Analog
<sup>95</sup> Mo	5	0.070	0.010	100	0.050	Counting
<sup>103</sup> Rh	5	0.001	0.010	100	0.050	Analog
<sup>111</sup> Cd	5	0.001	0.100	100	0.500	Counting
<sup>208</sup> Pb	5	0.120	0.010	100	0.050	Analog
Medium resolution, 80 scans						
<sup>59</sup> Co	100	0.001	0.010	20	0.200	Both
<sup>60</sup> Ni	100	0.001	0.005	20	0.100	Both
<sup>63</sup> Cu	100	0.001	0.005	20	0.100	Both
<sup>66</sup> Zn	100	0.001	0.010	20	0.200	Both
<sup>69</sup> Ga	100	0.001	0.002	20	0.040	Both

RF power: 1250 W; plasma gas flow: 13.1 min<sup>-1</sup>; auxiliary gas flow: 0.75 l min<sup>-1</sup>; nebulizer gas flow: 0.85–0.95 l min<sup>-1</sup> (optimized daily); sample flow rate: 0.5 ml min<sup>-1</sup> (during sample analysis).

The distance between the light source and the caps was ca. 7 cm.

Experiments were also carried out to optimize the UV oxidation time. Three of the samples with high DOC from the South Bay and metal standards spiked with EDTA were UV irradiated for times ranging from 15 min to 4 h and the trace metal concentrations determined using the CRCP-ICP-MS system.

#### 2.4. ICP-MS and flow injection system

All measurements were made with a Thermo-Finnigan Element magnetic sector ICP-MS using a Glass Expansion Conikal nebulizer and a Scott-type double pass spray chamber (cooled to 10 °C). Standard nickel cones were used. The nickel in the cones resulted in a consistent nickel blank of about 5 ng l<sup>-1</sup>. The instrument operating parameters and data acquisition details are reported in Table 2. Since there were small or no polyatomic interferences for Mn, Cd, and Pb, they were run at low resolution ( $r = 300$ ) using Rh as an internal standard. Co, Cu, Ni, and Zn had significant polyatomic interferences and were run at medium resolution ( $r = 3500$ ) using Ga as the internal standard.

The nebulizer gas flow was optimized daily to provide maximum counts for the <sup>103</sup>Rh or <sup>69</sup>Ga in the eluting acid. The output from the Finnigan  $\mu$ -sampler was connected directly to the ICP-MS flow chamber. The ICP-MS and FI system were both controlled

by the ICP-MS Element software. The Finnigan  $\mu$ -sampler program is shown in Table 3.

PTFE tubing (0.25, 0.5 and 0.8 mm. i.d., Upchurch Scientific Inc., Oak Harbor, WA) was used as transfer lines from peristaltic pump tubing and other connections. All connections and tees were 1/4–28 low pressure Tefzel flangeless fittings (Upchurch Scientific, Oak Harbor, WA). Toyopearl AF-Chelate 650 M resin (Tosohass, Montgomeryville, PA) was packed into a Global-FIA column (part #MC-1CNM, GlobalFIA, Fox Island, WA). The resin has a capacity of 35  $\mu$ mol ml<sup>-1</sup>. The 1 cm column consisted of a tapered inner chamber with frits at each end, which are push-fit into a threaded outer sleeve. A Watson–Marlow Pump-Pro MPL peristaltic pump (Watson–Marlow Bredel, Wilmington, MA) was used to remove waste from the nebulizer. A schematic diagram of the FI plumbing is presented in Fig. 1. Two-stop silicone tubing was used for all reagents and sample. The FI pumps were run at a higher speed during sample flushing and

Table 3  
 $\mu$ -Sampler program

Step	Duration (s)	Pump-1 (ml min <sup>-1</sup> )	Pump-2 (ml min <sup>-1</sup> )	Valve position
Condition	20	0	1.0	1
Flush	30	1.0	0	2
Load	60	1.0	0	1
Rinse	120	0	0.5	1
Elute	60	0	0.5	2

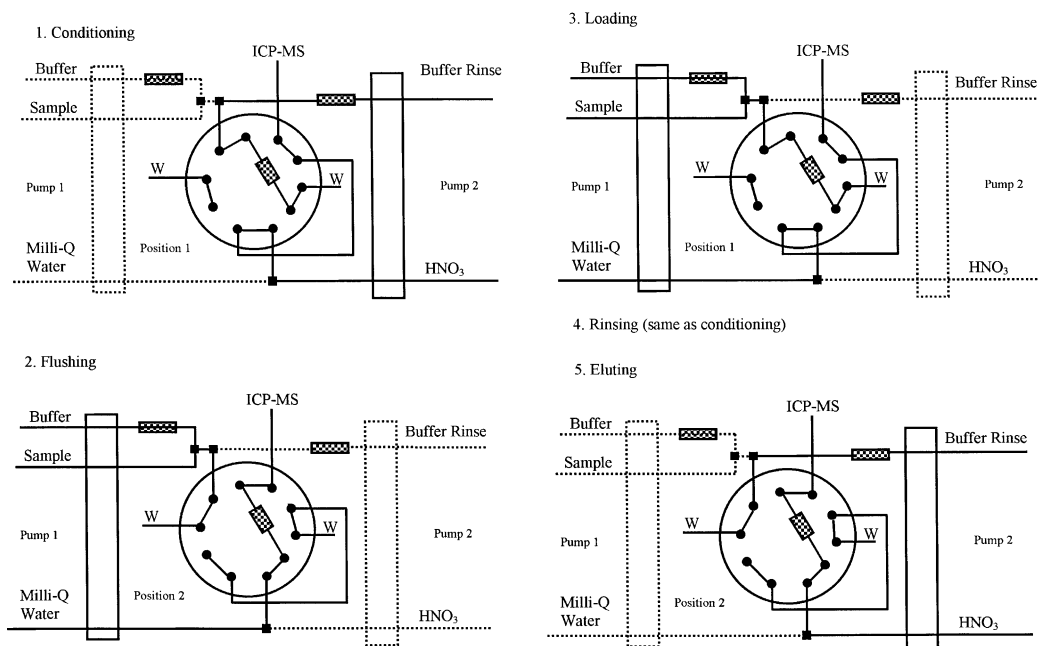


Fig. 1. Schematic diagrams of the flow injection system.

loading. Two additional 2 cm Global-FIA columns were packed with the iminodiacetate resin and installed in the buffer and wash lines after the pump to remove any metals in the buffer and rinse solutions and decrease subsequent blanks and detection limits.

### 3. Results and discussion

#### 3.1. Comparison of on-line CRCP-ICP-MS and SE-GFAAS

Water samples from the SFBE were analyzed by the CRCP-ICP-MS method. The water samples were collected from 12 sampling stations covering the major geographical regions of the estuary in spring 1993 and winter or summer 1995, and were reflective of the spatial and temporal variation of salinity and DOC in the estuary [37].

These water samples were filtered (0.22  $\mu\text{m}$ ) and acidified (HCl, pH:  $\sim$ 1.7–1.8) after collection and allowed to stand for a month. This, presumably, released the organic-bound and fine colloid-associated metals into solution before organic extraction using

PDC/DDC, and final analysis by GFAAS or the on-line CRCP-ICP-MS method.

Fig. 2 shows the trace metal concentrations for samples determined by on-line CRCP-ICP-MS and by SE-GFAAS. There is good agreement between the two methods for cadmium, lead, manganese, and zinc. However, the concentrations of copper, cobalt and nickel determined by on-line CRCP-ICP-MS are 13–20% lower compared to those of SE-GFAAS.

Before PDC/DDC (or CRCP) extraction, the pH of the sample was adjusted to ca. 5.0 with an acetate buffer. There is, therefore, a risk of the trace metals recombining with any organic ligands in solution to form soluble metal–ligand complexes. In the case of organic extraction, a large excess of strongly chelating ligands (PDC/DDC) is added to the sample at the same time as the pH adjustment. This is to ensure that the metals of interest all form bis-complexes with the dithiocarbamates rather than re-complexing with any natural ligands. Chloroform is then added and the sample is shaken for 3 min and allowed to stand for another 5 min for phase separation. The potential of metals to re-complex with natural ligands in the on-line CRCP-ICP-MS method is reduced by

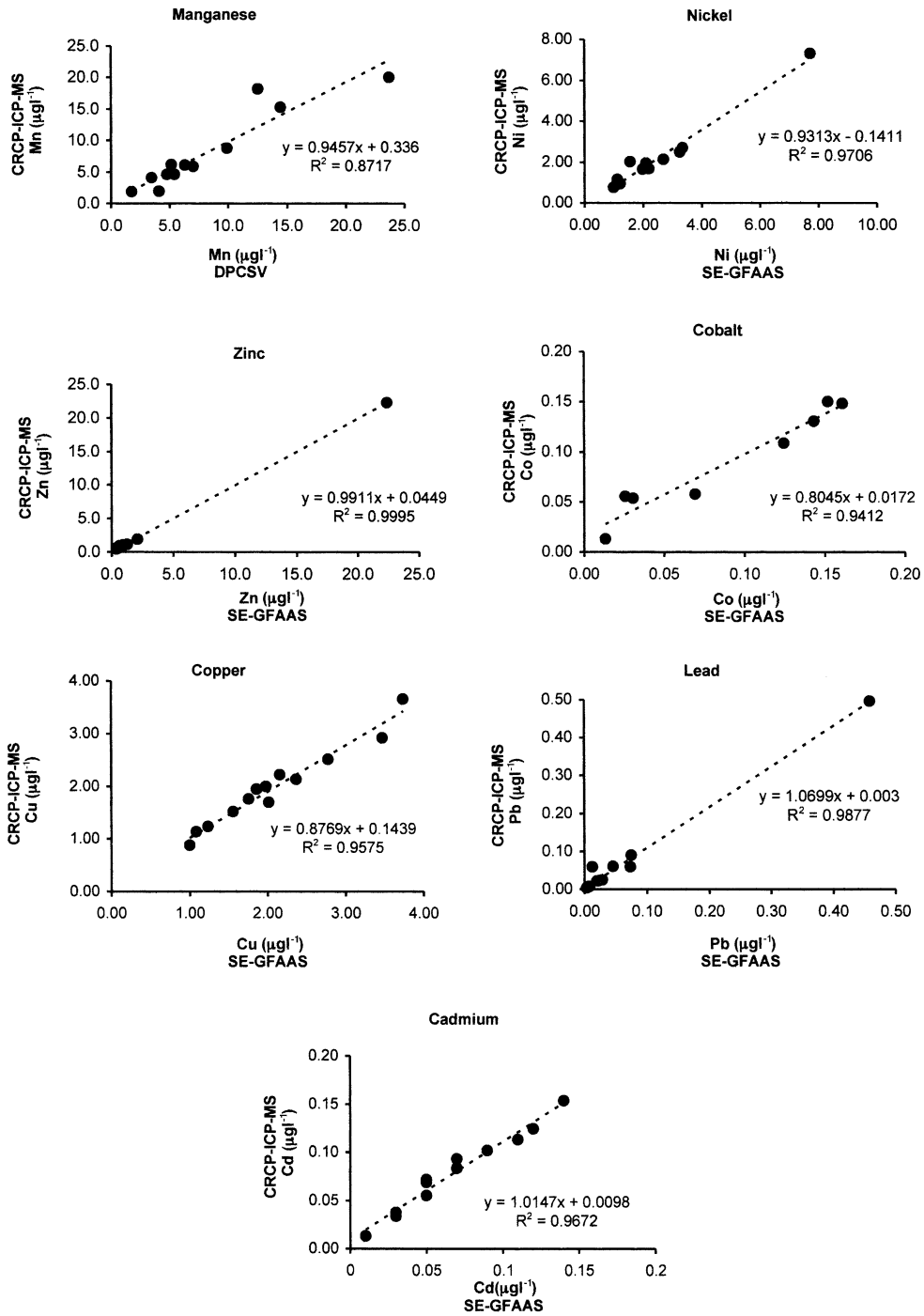


Fig. 2. Comparison of trace metal concentration measurements of estuarine water samples analyzed by SE-GFAAS and on-line CRCP-ICP-MS.

buffering the acidified sample on-line for less than 3 s before the buffered sample reaches the iminodiacetate resin. However, there is still a risk of a small fraction of the metal re-complexing with the organic ligands in this short time and thus going through the column undetected, especially so for copper and cobalt which have fast reaction kinetics and are strongly complexed by organic ligands.

### 3.2. Effect of organic complexation on on-line CRCP-FI-ICP-MS analysis

To investigate this possibility, we spiked both estuarine water certified reference material (CRM) (SLEW-3) and a trace metal standard with 100 nM of EDTA, and then ran it through the on-line CRCP-ICP-MS method. The SLEW-3 CRM is also preserved acidified and the metals would therefore not be expected to complex with EDTA in the acidified sample. Table 4 shows the concentration of the metals determined from that analysis.

More than 99% of copper, 83% of zinc and 10% of cobalt were not extracted by the resin from the Mill-Q standards in the presence of 100 nM EDTA. Similarly, about 70% of copper and 5% of cobalt could not be extracted from the estuary CRM in presence of 100 nM EDTA. Although the composition and concentration of DOC in estuarine water samples might not be known, several studies have indicated the presence of strong copper, cobalt and zinc binding ligands [2–4,13]. Some of the trace metal complexing ligands,

especially in heavily urbanized estuaries like the San Francisco Estuary, also contain high levels of anthropogenic ligands such as EDTA [10].

### 3.3. UV oxidation

In order to destroy the majority of the DOC and, in particular, any metal complexing ligand, we subjected the samples to UV digestion using a Hg lamp. Fig. 3 shows the effect of UV digestion time on the concentration determined for cobalt, copper, nickel and zinc in three of the estuarine samples and EDTA-spiked standards. The two samples (BA05 and BA30) chosen for the UV digestion optimization had the highest DOC concentrations and were both from the South San Francisco Bay.

UV oxidation was quite effective in destroying the ability of the synthetic complexing agent, EDTA, to interfere with the isolation of the metals in the standards and any other metal complexing organic ligands in less than 1 h. The recovery of both copper and cobalt from the EDTA spiked SLEW-3 CRM was also quantitative after 1 h of UV digestion.

### 3.4. On-line CRCP-ICP-MS analysis of samples after UV digestion

Fig. 4 shows a comparison of SE-GFAAS measurements with those determined by on-line CRCP-MS after UV oxidation. While the slope for cobalt and copper showed much improved agreement between the two methods after UV digestion ( $1.002 \pm 0.117$  and  $1.009 \pm 0.049$  compared to  $0.805 \pm 0.081$  and  $0.874 \pm 0.058$ ,  $P = 0.05$ , before UV oxidation for cobalt and copper, respectively), in contrast, there was no improvement for nickel between the SE-GFAAS and On-line CRCP-ICP-MS even after 4 h of UV oxidation. At first, we attributed this effect to incomplete destruction of the DOC in the sample by UV degradation, and tried UV oxidation of samples with addition of hydrogen peroxide [30]. However, there was still no significant ( $P = 0.05$ ,  $t$ -test) difference in nickel concentration with the addition of hydrogen peroxide even after 4 h of UV irradiation.

We propose three possible explanations for the latter: (1) the estuarine samples contained nickel-specific organic complexing ligands that could not be destroyed with the extensive UV oxidation (even

Table 4

Trace metal concentrations in the National Research Council of Canada certified estuarine water reference material, SLEW-3 and metal standards ( $3 \mu\text{g l}^{-1}$ ) spiked with 100 nM EDTA and analyzed by on-line CRCP-ICP-MS method

	Recovery (%)	
	SLEW-3	Standard
Cadmium	107	N/A
Cobalt	95	89
Copper	31	1
Manganese	101	N/A
Nickel	99	102
Lead	116	N/A
Zinc	104	17

N/A: not analyzed.

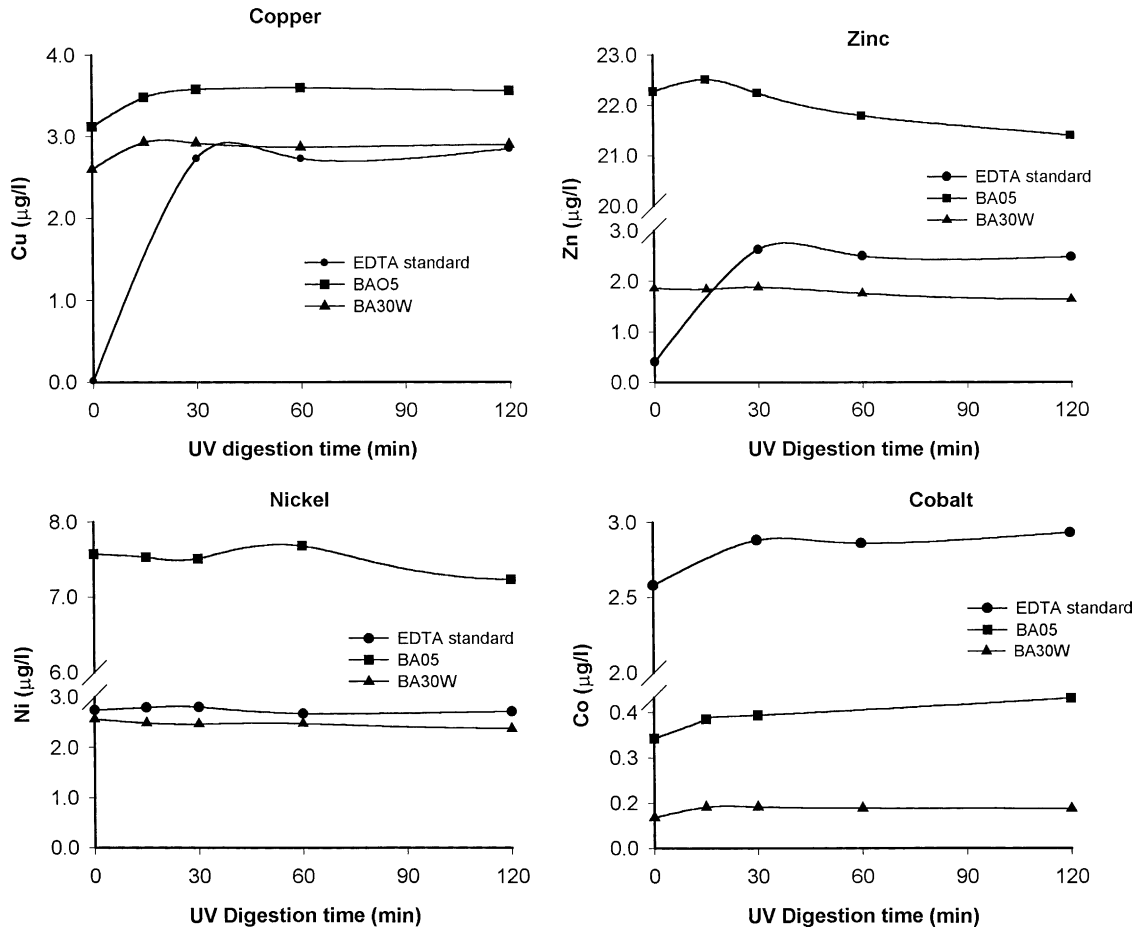


Fig. 3. Effect of UV digestion time on metal concentration determined by on-line CRCP-ICP-MS for trace metal standard solution ( $3 \mu\text{g l}^{-1}$ ) spiked with  $100 \text{ nM}$  EDTA and two estuarine water samples from South San Francisco Bay in 1995 with DOC concentrations of  $5.5 \text{ mg l}^{-1}$  (BA05) and  $3.3 \text{ mg l}^{-1}$  (BA30).

in the presence of hydrogen peroxide) and hence re-complexed the nickel in the 3 s interval before contact with the resin; (2) there are strong nickel–ligand complexes existing in the acidified ( $\text{pH } 1.5$ ) water samples; and (3) the 15–20% difference in nickel concentration between SE-GFAAS and on-line CRCP-FI-ICP-MS was due to instrumental measurement uncertainties. The first explanation is unlikely since nickel complexation reactions are known to be quite slow [38]. The second is also unlikely since such stable complexes of nickel would also be most likely not extracted by the thiocarbamate ligands as well. The third, and most likely, explanation is instrument uncertainties in the measurements. The CRCP-ICP-MS nickel concentra-

tion measurements (mean  $\pm$  S.D.) were constantly at the low end ( $1.11 \pm 0.01 \mu\text{g l}^{-1}$ ,  $n = 3$ ) of the recommended SLEW-3 CRM values ( $1.23 \pm 0.07 \mu\text{g l}^{-1}$ ); and the corresponding SE-GFAAS values for near shore seawater CRMs, CASS-2 ( $0.33 \pm 0.01 \mu\text{g l}^{-1}$ ,  $n = 3$ ) and CASS-3 ( $0.40 \pm 0.01 \mu\text{g l}^{-1}$ ,  $n = 2$ ) were on the high end of the certified values of ( $0.30 \pm 0.04 \mu\text{g l}^{-1}$ ) and ( $0.39 \pm 0.06 \mu\text{g l}^{-1}$ ) for CASS-2 and CASS-3, respectively. This difference in nickel recovery from the two CRMs determined by SE-GFAAS and CRCP-ICP-MS does not, however, explain the positive correlation ( $R = 0.89$ , simple linear regression, excluding sample BA05) of the difference in nickel concentration determined by

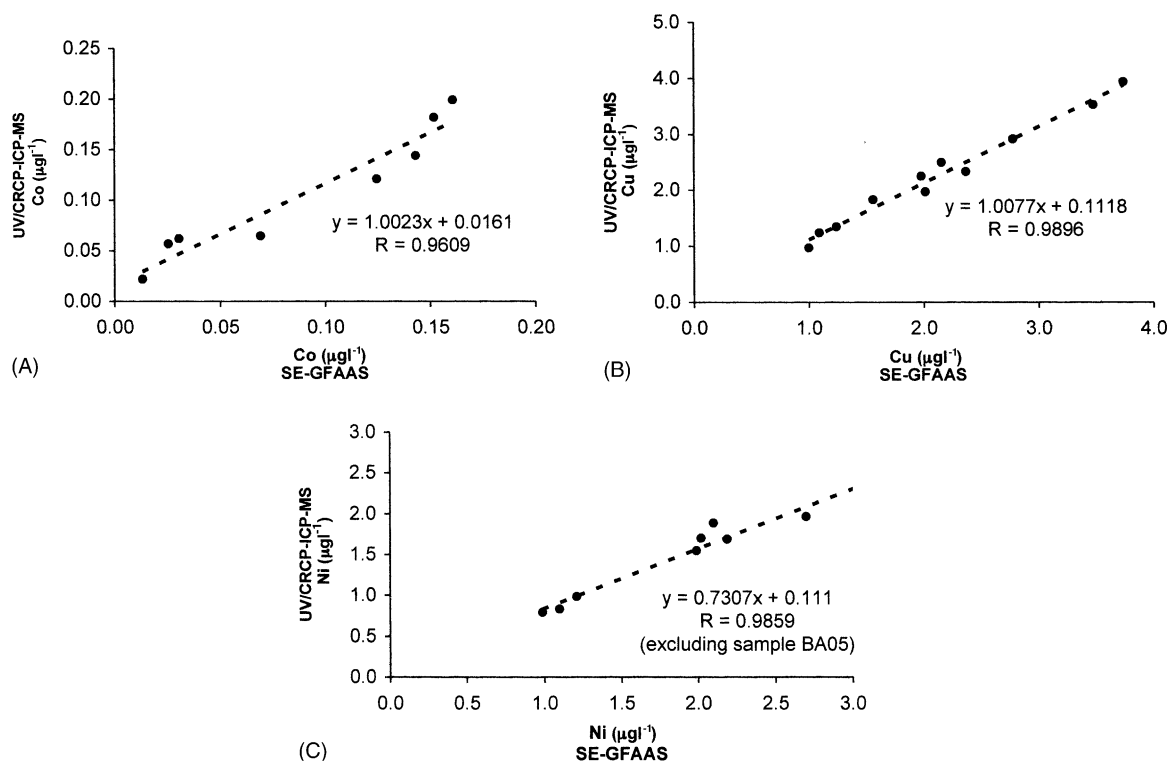


Fig. 4. Comparison of (A) cobalt, (B) copper, and (C) nickel (excluding sample BA05) concentration measured by the on-line CRCP-ICP-MS method and, after UV digestion, by SE-GFAAS. Copper and nickel samples were collected in 1995 and cobalt samples in 1993 (Table 1).

SE-GFAAS and those determined by CRCP-ICP-MS, with the DOC.

### 3.5. Relationship with DOC

The composition of DOC in the estuarine water samples is complex and is thought to include humic acids, fulvic acids, glycollic acid, peptides, proteins, amino acids, lipids and polysaccharides [14]. In heavily urbanized and industrialized estuaries like San Francisco, DOC include anthropogenic complexing agents such as EDTA, phosphonates, citric acid, tartaric acid and surfactants [6]. This is especially so in the southern reach of the SFBE (BA05, BA30, BA40, BB70) which is the most industrialized and urbanized part of the estuary, where most of the samples with high DOC concentrations were collected.

In contrast to the phosphate substitute NTA, EDTA is not eliminated in significant amounts during wastewater treatment either by biological nor

by physical–chemical processes [39,40]. Bedworth and Sedlak [10] measured up to 2  $\mu\text{M}$  of EDTA in wastewater effluents from a water pollution control plant, near station BA05. Fig. 5 shows the difference in copper and cobalt concentration determined by CRCP-ICP-MS before and after UV digestion.

There is a positive correlation for cobalt ( $R = 0.95$ ) and copper ( $R = 0.81$ ) between this difference and the DOC concentration. It is assumed that the difference represents the organically complexed fraction of the metal made available by UV destruction of the corresponding complexing organic ligands. That some samples with a high DOC did not necessarily show strong copper and cobalt complexation demonstrates the importance of DOC composition. For example, sample BF-20 (spring 1993) was collected from the North Bay, which receives most of the DOC from riverine inputs most likely humic substances with negligible anthropogenic or phytoplankton sources [41].

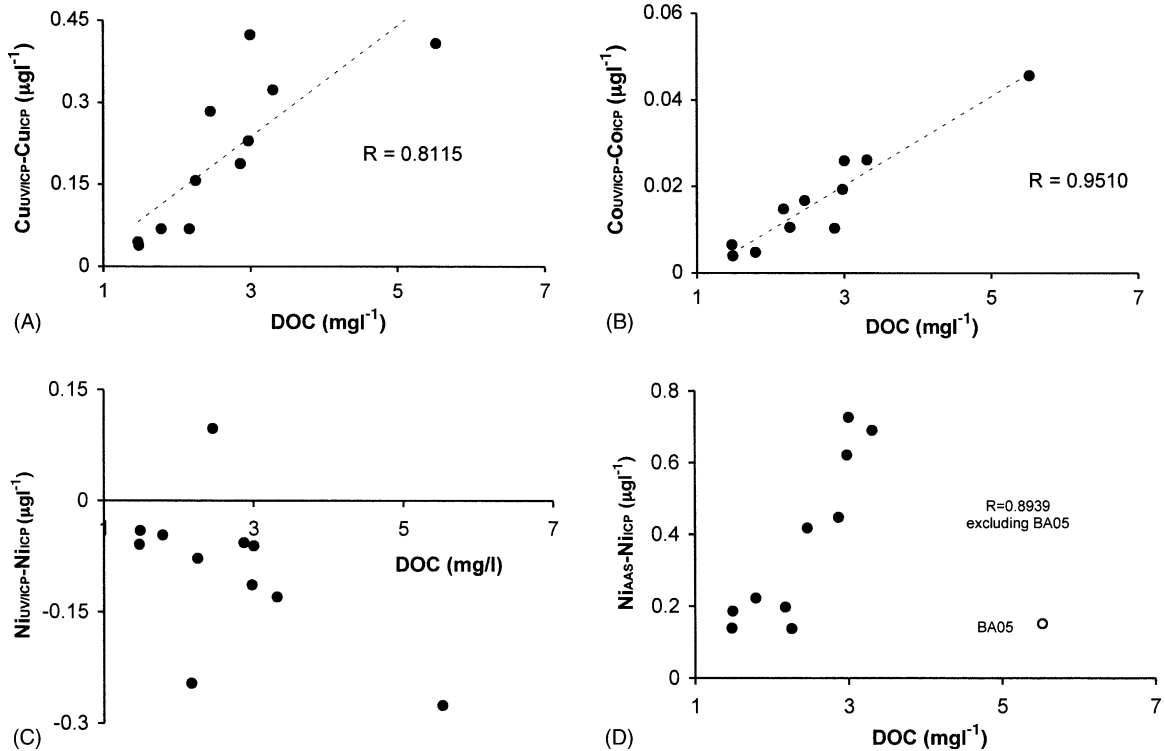


Fig. 5. Difference in metal concentrations determined by on-line CRCP-ICP-MS before ( $M_{ICP}$ ) and after ( $M_{UV/ICP}$ ) UV digestion of SFB estuarine water samples and their DOC concentration for: (A) copper, (B) cobalt, and (C) nickel. The difference in nickel concentrations determined by SE-GFAAS and those determined by on-line CRCP-ICP-MS are plotted against their DOC concentrations (D). Notice that although there is a positive correlation in the difference in nickel concentration between the two methods and DOC, there is no direct correlation in the difference in nickel concentration determined by CRCP-ICP-MS before and after UV oxidation (cf. (A) and (B)).

The results for nickel are interesting because although there is a positive correlation with DOC concentration, the concentration of nickel determined by CRCP-ICP-MS before and after UV digestion (even with hydrogen peroxide pretreatment) remains the same (Fig. 5C and D). The exact explanation for this is not clear.

#### 4. Conclusion

This study has demonstrated the need for more investigations on the performance of new CRCP-based methods for the analysis for total dissolved trace metals in estuarine water samples.

It has been shown that organic complexation is an important factor to consider in the analysis of to-

tal dissolved trace metals by CRCP sample pretreatment methods prior to on-line ICP-MS determination. The need to buffer acidified samples to  $pH \geq 5$  may introduce the risk of a small fraction of the metal re-complexing with the organic ligands and thus going through the column undetected. This is especially so for metals such as copper and cobalt, which have fast reactions and are strongly complexed by ambient concentrations of strong metal-binding dissolved organic ligands. UV digestion is a clean and efficient way of destroying the organic ligands with minimal risk of sample contamination.

This study has also demonstrated the importance of carrying out more detailed investigations involving a large and representative sample set that reflects the complexity of estuarine systems. The observations in this study would not have been evident from simple

assessment of the method performance with an estuarine CRM or a small set of samples. A variety of samples representative of the spatial and even temporal variation of the SFBE was necessary to detect these trends.

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