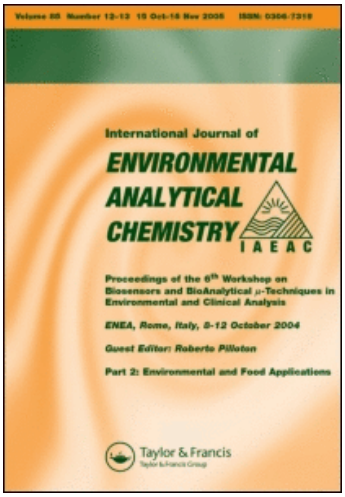

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A FIELD METHOD FOR THE DETERMINATION OF COPPER IN ESTUARINE WATERS

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A precise and sensitive solvent extraction-colourimetric technique has been developed for the determination of dissolved copper in saline waters, using a reagent of established selectivity. The limit of detection and operating range of the technique have been improved to cover copper concentrations found in estuaries and contaminated coastal waters. The limit of detection of the technique is estimated as 0.5 $\mu g\ l^{-1}$. Data for spiking recovery and long term standard deviation of determination are reported. Analytical data produced by this technique for over forty estuarine samples are compared with corresponding analyses by graphite furnace atomic absorption spectrophotometry.

Keywords: Copper determination; estuarine water; coastal water; saline water; neocuproine; solvent extraction

INTRODUCTION

The widespread use of copper and its salts and its relatively high toxicity to aquatic life make it one of the most important trace metal contaminants in natural waters. Copper contamination in estuarine waters is of increasing concern. The effect of industrial discharges, diffuse sources (including leaching into sewage effluent from domestic water systems) and the increased use of copper-based antifoulant products for small boats combine to increase estuarine copper concentrations from the background coastal water value of 200 – 500 $ng\ l^{-1}$ to levels of several $\mu g\ l^{-1}$. In enclosed marinas or where dilution is restricted, concentrations can be as high as 10 $\mu g\ l^{-1}$. Copper is classified as a List II substance in the European Union Dangerous Substances Directive (76/464/EEC). An Environmental Quality Standard (EQS) of 5 $\mu g\ l^{-1}$, expressed as an annual average con-

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centration, has been set for dissolved copper in coastal and estuarine water. This establishes the need for routine monitoring to assess compliance with this limit value. An appropriate analytical technique for compliance monitoring should be capable of achieving a limit of detection of at least 1 μg/l, preferably one tenth of the EQS value.

Current monitoring tends to be carried out using instrumental techniques such as graphite furnace atomic absorption spectrometry (GFAAS) or inductively-coupled plasma mass spectrometry. These laboratory-based techniques possess the required sensitivity but suffer from serious interferences from the salt matrix of marine samples. This means that the methodology must include a preliminary separation step – for example by solvent extraction or ion exchange[1]. Such sample pre-treatment increases the complexity of analysis, limits sample throughput and increases costs. The use of voltammetry has been advocated as suited to saline matrices[2]. The drawbacks of this approach are its relative complexity and the fact that it is subject to matrix interference by complexing substances present in estuarine waters. Alternative approaches to analysis, such as colorimetry, use simpler instrumentation and are not so affected by the sample matrix. However, until now lack of sensitivity has limited the use of colorimetry for the analysis of natural waters. Provided improved sensitivity can be achieved, colorimetry can offer benefits including: the ability to undertake analysis in the field - as an aid to ad-hoc surveys and site investigations; low capital equipment costs; and flexibility in setting up the method. At least for small batches of analysis, colorimetry can also achieve a sample throughput equivalent to that of more complex instrumental techniques. This paper describes a procedure which was developed and tested with the aim of realising these benefits.

Target performance

The following performance criteria were defined[3,4] as desirable in a method to be used for estuarine monitoring, assuming that it is necessary to operate in the range 0–10 μg l^{-1} and that the establishment of compliance with a Quality Standard of 5 μg 1^{-1} is of primary interest.

- the standard deviation of individual results should be less than 5% of the determinand concentration or 0.25 μg 1^{-1}, whichever was the larger;
- spiking recovery (both saline and deionised water) should not be significantly outside the range 95–105%;
- the limit of detection should be 1 μg 1-^{1} or better.

Approaches to colorimetry

The principal constraints in selecting a colourimetric technique are the need for both selectivity and adequate sensitivity. In the case of copper, there are several potential techniques available. The most promising methods employ the reagents bathocuproine, neocuproine and bis-cyclohexanone oxalyldihydrazone. The first two rely on the "ferroin" chromophore and are noted for their selectivity for copper (Cu) but they do not possess the required sensitivity when used for direct determinations in aqueous solution. Reported limits of detection[5,6], would not meet the above target. The reaction between copper and bis-cyclohexanone oxalyldihydrazone is insufficiently sensitive and colour development is rather dependent on reaction temperature[7]. More recent work on colorimetry has sought to improve sensitivity using techniques such as micro- ion-exchange[8], or solid phase supported solvent extraction[9,10]. Whilst these techniques have much to offer in research applications, we felt that a simpler solvent extraction approach was likely to prove more widely applicable.

The reagent neocuproine was selected because its copper complex is most readily extractable into an organic phase, with concomitant preconcentration and increased sensitivity. Extraction into chloroform has been suggested as a means of improving sensitivity, but no adequately validated methodology has been reported. The use of chloroform is now discouraged in most modern laboratories, so a more acceptable alternative solvent was sought. Extraction into 4-methyl pentan-2-one proved fruitless; partitioning into dichloromethane was more promising.

EXPERIMENTAL

Reagents

Neocuproine reagent: dissolve 1.0g neocuproine (Merck, Poole, UK) in 100 ml methanol (stable for a month, stored under refrigeration). Hydroxylamine hydrochloride solution – dissolve 50g (Merck "Aristar", Poole, UK. or equivalent grade) in 400 ml deionised water (prepare fresh weekly). Acetate buffer: add 42g sodium acetate, plus 35g glacial acetic acid (both Merck "Aristar" or equivalent grade), to a polyethylene bottle and make up to 500 ml. Adjust buffer to pH 4.7±0.2 with additions of M NaOH or M HCl) (stable for a month, stored under refrigeration). Ammonia solution: 10% v/v concentrated ammonia solution (specific gravity 0.880), (stable for a month, stored under refrigeration).

Method

All water was deionised and all chemicals were of Reagent Grade. All apparatus was presoaked in 5% v/v nitric acid and rinsed with deionised water (DIW) before use.

80 ml sample were dispensed using a measuring cylinder into a 250 ml polyethylene bottle (Nalgene low density polyethylene, narrow neck). The pH value of an unpreserved sample was adjusted to 4.7 ± 0.2 by addition of 0.5ml of 0.5 ml of acetate buffer (0.5 ml). Samples preserved with nitric acid were treated with 0.5 ml of buffer and sufficient ammonia solution to achieve a pH value of 4.7 (a separate portion of sample was checked using a pH meter). Then 5 ml hydroxylamine solution was added, followed by 1 ml neocuproine reagent and 5 ml dichloromethane. The mixture was shaken vigorously for 3 min. A portion of the dichloromethane layer was separated using an autopipette and transferred to a 4cm slotted cell (Jencons, Leighton Buzzard, UK). The absorbance of the extract was measured at 457 nm. A calibration curve of absorbance versus concentration by analysis of a blank and standard solutions of 2, 5 and 10 $\mu g\ l^{-1}$, prepared by dilution of a stock solution (diluting Merck Spectrosol (1000 mg l^{-1})) was established using deionised water.

The slotted cell provides a 4cm path length but only requires 2 ml of extract (compared with more than 5 ml for a conventional rectangular cell). For laboratory use, the spectrophotometer used was a Cecil model 2125. Performance data reported below refer to data obtained on this instrument. For field use, a similar portable absorptiometer was employed, though this needed to be modified to provide readings to 0.001 absorbance.

RESULTS AND DISCUSSION

The calibration line was linear to a concentration of 10 $\mu g\ l^{-1}$. The equation $y=11.7x + 9.7$ illustrates a typical calibration, where "y" represents absorbance in milli-absorbance and "x" concentration in $\mu g\ l^{-1}$. The use of extraction (shaking) times between 1 and 8 minutes had little effect on absorbance. Tests on seawater samples spiked to 10 $\mu g\ l^{-1}$ at 10°C and 23°C gave essentially the same result (10.1 and 9.6 $\mu g\ l^{-1}$, respectively) when read off a calibration line prepared in standard solutions at 23°C.

The precision and recovery of analysis were examined as recommended in the relevant ISO Standard[10]. Multi-batch performance tests were performed in which duplicate determinations were made on: independently prepared blanks; standard solutions – low and high in the concentration range of interest; and, two

seawater samples of relevant concentrations (Table I). Seven batches of analysis were sufficient to provide the 10 degrees of freedom for overall (total) standard deviation recommended[11,12] as conferring an acceptable level of reliability. Recovery data were calculated by comparison with the nominal values for the independently prepared standard solutions. For the seawater samples, recoveries were assessed with respect to the mean reported value established when these samples had been used in an interlaboratory test.

TABLE I Precision data for the method (7 batches of analysis) units: $\mu g\ l^{-1}$

	Blank	*Low standard (DIW) ($2\mu g l^{-1}$)*	*High standard (DIW) ($10\mu g l^{-1}$)*	*Sample 1 (seawater) ($1.5\mu g l^{-1}$)*	*Sample 2 (seawater) ($3.5\mu g l^{-1}$)*
Mean	0.06	2.11	9.6	1.58	3.8
S_w	0.10	0.17	0.42	0.14	0.21
S_b	0.10	0.14	0.24	0.09	0.13
S_t	0.14	0.22	0.49	0.17	0.24
degrees of freedom of S_t		10	12	11	12
Recovery %		103 ± 9	96 ± 3	102 ± 3	109 ± 5
limit of detection	0.5				

S_w = Within batch standard deviation
S_b = Between batch standard Deviation
S_t = Total standard deviation
DIW = Deionised water

The importance of systematic errors prompted us to undertake a more extensive examination of bias by comparing the results of this technique with those obtained using an established published method[13] based on micro-solvent extraction-GFAAS. Samples (120 ml) collected from the estuaries of the the river Orwell (Suffolk, UK) and Hamble (Hampshire, UK) and associated marinas were filtered through an acid washed/deionised water rinsed 0.45 μm cartridge filter. These filtered samples were acidified to 0.2% v/v with respect to nitric acid. Portions of each sample were analysed by the established technique of micro-extraction GFAAS. The samples were of salinity in the range 20 to 35 parts per thousand, owing to the relatively small freshwater inputs in both estuaries.

The remaining portions of each sample were analysed using the above technique. Figure 1 illustrates the comparison between the results obtained. Since the data produced by colorimetry and those produced by GFAAS are both subject to

variation, it is not appropriate to use conventional linear regression to assess the degree of agreement between the two sets of data. Instead a non-parametric regression technique known as Theil's method[14] was used. The resulting regression line (of colorimetry on GFAAS) was of slope 1.09 with confidence limits (p=0.05) from 0.96 to 1.3. The intercept was 0.18, with confidence limits (p=0.05) from –0.11 to 0.39. This indicates no significant difference can be detected between the two techniques.

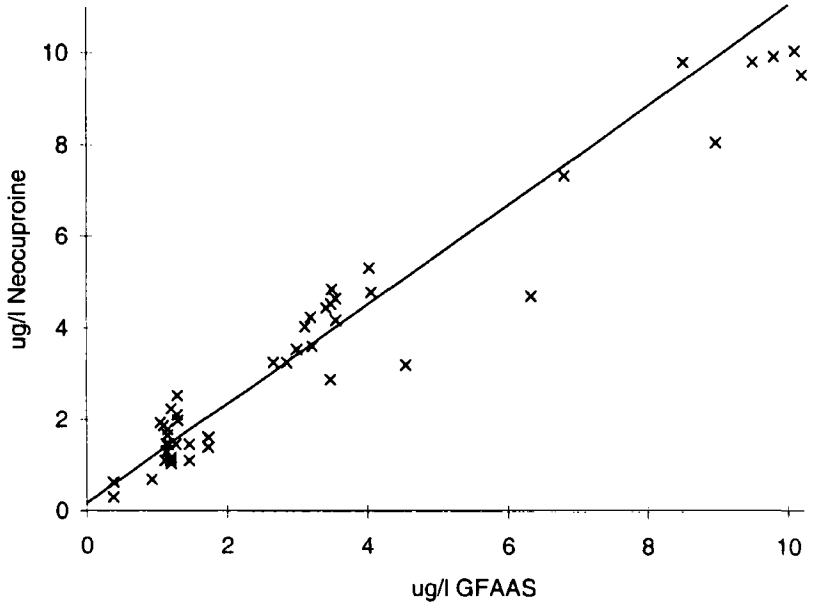

FIGURE 1 Comparison between neocuproine colorimetry and microsolvent extraction **GFAAS** Samples from two UK estuaries were analysed by both techniques. The solid line is the non-parametric regression line between the two sets of data

CONCLUSIONS

This complexation/preconcentration procedure is capable of determining dissolved copper in saline samples to a detection limit of 0.5 $\mu g\ l^{-1}$ with a freedom from random and systematic error adequate for compliance monitoring in coastal and estuarine waters. Recoveries of copper from both deionised water and full saline samples (35 parts per thousand) were not significantly outside the range 95–105%. Data have been shown to be comparable to results obtained using another established method. The technique is relatively simple to use and is

suited to use in the field as an aid to ad-hoc surveys and site investigations. It utilises inexpensive and readily available chemicals and requires instrumentation available in most laboratories world-wide. It offers a cheap and simple alternative to more complicated (and more expensive) analytical techniques.

References

[1] *Methods for the Examination of Chemical Substances in Marine and Estuarine Environmental Samples*, EPA Report No. EPA/600/R-92–12 (1992).

[2] The determination of twelve trace metals in marine and other waters by voltammetry or AAS. Published by the Standing Committee of Analysts, In *Methods for the examination of waters and associated materials*, Her Majesty's Stationery Office, (1987).

[3] J. Timmerman, M.J. Gardner and J.E. Ravenscroft. UN/ECE Task Force on Monitoring and Assessment, Volume 4 – Quality Assurance. (1996).

[4] R.V. Cheeseman, M.J. Gardner and A.L. Wilson. *A Manual on Analytical Quality Control for the Water Industry*. WRc report NS30. (1989).

[5] E.B. Sandell and H. Onishi. *Photometric Determination of Traces of Metals*, 4th edition (John Wiley, Chichester, 1978). 1082 pp.

[6] American Public Health Asssociation, *Standard Methods for the Examination of Water and Wastewater*, 19th edition. (1995).

[7] Department of the Environment Standing Committee of Analysts Analysis of Raw, Potable and Waste Waters. Her Majesty's Stationery Office, London pp 303. (1972).

[8] K. Yoshimura, S. Nigo and T. Tarutani.. *Talanta*, **29**, 173–176. (1982).

[9] T. Kasahara, N. Ogawa, S. Hata, K. Taguchi, M. Goto, K. Ohta and K. Ohzeki. *Water Res.*, **23**, 933–936. (1989).

[10] T. Saito. *Talanta*, **41**, 811–815 (1994).

[11] ISO/TR 13530 Water Quality. *Guide to Analytical Quality Control for Water Analysis* (1998).

[12] Department of the Environment, Transport and the Regions. *Guidance on Safeguarding the Quality of Public Water Supplies* (HMSO, London, 1990) 108 pp.

[13] S.C. Apte and A.M. Gunn. *Anal. Chim. Acta* **193**, 147–156. (1987).

[14] J. C. Miller and J. N. Miller. *Statistics for Analytical Chemistry* (Ellis Horwood, Chichester, UK, 1984) 202 pp.