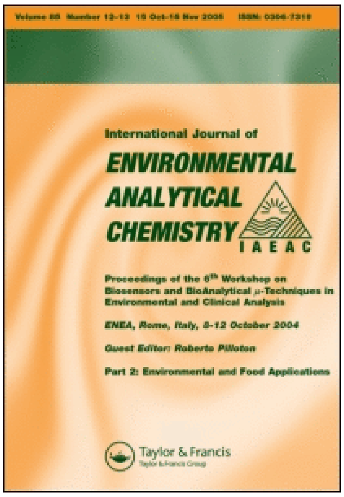

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RAPID DETERMINATION OF ZINC IN SALINE WATERS

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A rapid, precise and sensitive solvent extraction-atomic spectrometric technique has been developed for the determination of dissolved zinc in saline waters, using a well established solvent extraction-flame atomic absorption spectrometry method (ammonium pyrollidine dithiocarbamate – methyl isobutyl ketone). The concentration range of the technique covers levels found in estuarine and coastal waters for analytical batches of 22 samples. The limit of detection of the technique is estimated as 0.7 µg L^{-1}. Data for spiking recovery and long term standard deviation of determination are presented.

Keywords: Zinc; estuarine water; coastal water; saline water; flame atomic absorption spectrometry; solvent extraction

INTRODUCTION

Zinc is ubiquitous in surface waters. It is classified as a List II substance in the Dangerous Substances Directive (76/464/EEC); consequently it is routinely monitored in estuarine and coastal waters to assess compliance with EU environmental quality standards (40 µg/l for estuarine and coastal waters). Typical concentrations in uncontaminated waters in the UK are around 0.5 – 1 µg L^{-1}. In areas subject to industrial discharges concentrations can be elevated to levels of up to 10 µg L^{-1}.[1] To identify waters that are subject to zinc contamination, an analytical technique should be capable of achieving a limit of detection of at least 1 µg/l. In saline waters, zinc can be determined by direct aspiration flame atomic absorption spectrometry (FAAS) to a detection limit of approximately 5 µg/l. At these levels, however, control over random and systematic error can be degraded due to interferences by the sample matrix. Consequently, direct determination by

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FAAS may not be sufficiently sensitive to monitor zinc in estuarine and coastal waters. Although atom trapping FAAS is capable of achieving limits of detection in the region of 0.3 µg/l in river and estuarine water,[2] this technique is not always available for routine analytical laboratories. Furthermore, its precision (standard deviation of analysis). Other methods for the determination of zinc in saline waters include: electrochemistry,[3] which is rarely used as a routine method due to its complexity and propensity to contamination and current lack of automation; Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), which, although it offers a low limit of detection (eg 0.01 µg/l),[4] is expensive and can be subject to matrix interferences.[5] Other analytical techniques, such as liquid-phase polymer-based retention,[6] claim to offer a detection limit of 0.03 µg/l, but precision (standard deviation of 6 and 10% for drinking water and river water, respectively) again, may not be sufficient for environmental monitoring purposes.

Extraction/preconcentration, followed by atomic absorption spectrometry (generally FAAS) offers important advantages. The technique overcomes the two main difficulties in determining trace elements in complex matrices such as saline waters, by separation of the determinand from the sample matrix, whilst simultaneously achieving a preconcentration. Extraction can be accomplished either by solid phase adsorption, followed by elution and aspiration into FAAS, or by chelation of the determinand followed by solvent extraction / FAAS[6,7,8]. The complexity of some extractions (eg those using dithizone requiring pH adjustment, multiple extractions and evaporation to obtain satisfactory recovery) to achieve a limit of detection of 0.6 µg/l,[8] makes some these methods less applicable for routine application. Other methods require large volumes of both sample (500 ml) and solvent (30 ml) in order to achieve the required degree of preconcentration.[9]

There is, therefore, a need for a simple, precise and sensitive method capable of identifying zinc contamination in coastal waters. This paper describes the application of chelation by ammonium pyrollidine dithiocarbamate (APDC) in conjunction with solvent extraction (methyl isobutyl ketone (MIBK)), to provide a relatively quick and inexpensive flame AAS technique, capable of determining zinc concentrations in batches of up to 22 saline samples. Although APDC extraction into MIBK has been a well established method for determining trace metals in water,[10] there are no methods currently published that describe its use, with accompanying analytical performance data, for the routine determination of large batches of samples for zinc in natural waters.

EXPERIMENTAL

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. The ubiquitous nature of zinc in the environment required the utmost care and attention when performing sampling and filtration procedures. All samples were collected from estuarine and coastal sites, in acid-washed polyethylene bottles and filtered on-site under positive nitrogen pressure through acid-washed Nuclepore cellulose acetate filters (0.45 μm, 47mm diameter). The samples were preserved using AristaR nitric acid (17M) to a concentration of 0.2% (equivalent of 2ml of nitric acid added to each litre of sample). The importance of filtering samples in order to obtain 100% recovery of zinc, during the complexation/solvent extraction step, has been highlighted elsewhere.[11] Samples were then transferred to acid-washed high density polyethylene bottles and acidified to 0.2% nitric acid (Merck, AristaR).

The analytical reagent was prepared by dissolving 1.0 (+/- 0.1g) of APDC (Sigma Chemicals) and 5.3 (+/- 0.1g) of sodium hydrogen carbonate (Merck) in 500 ml of deionised water. This reagent was then decanted into a clean polyethylene bottle and purified by shaking with 20ml (+/- 1ml) 1,1,1 trichloroethane (Merck AristaR or equivalent) for 5 minutes. Merck Spectrosol or equivalent standards were prepared by diluting Merck Spectrosol (1000 mg/l) standards with deionised water containing 2 ml/l of nitric acid to concentrations of 0, 12.5, 25.0, 37.5 and 50.0 μg-Zn/l.

Extractions were performed in batches of 24 samples. These included seawater control samples of known concentration. For the purpose of performance testing, deionised water samples spiked with two zinc different concentrations (5 and 20 μg/l) were also included.

Aliquots (60g +/- 0.2g) of sample were weighed into 100ml volumetric flasks (100ml polypropylene volumetric flasks (Nalgene)). Weighing the samples directly into the flasks avoided unnecessary transfer of the sample into the flask via a measuring cylinder, hence reducing the possibility of contamination). Reagent (15 ml) was added, followed by 6 ml of the MIBK. The flasks were then shaken for 5 minutes in order to transfer the Zn-APDC complex from the aqueous to the solvent phase. Finally DIW was added to bring the MIBK up into the neck of the flask to facilitate aspiration into the flame AAS instrument. Analysis was performed immediately after extraction, although the Zn-APDC complex has been shown to be stable for at least 24 hours,[7] provided the MIBK is prevented from evaporating. All determinations were made on a Philips PU9200 flame (air/acetylene) atomic absorption spectrometer at 219.0 nm, with a 0.5nm bandpass. Background correction was carried out using a deuterium lamp.

RESULTS AND DISCUSSION

The method was used for the routine determination of dissolved zinc in estuarine and coastal samples collected from around the south east of England. In each batch of analysis, samples were prepared to assess the performance of the technique. These included Quality Control (QC) samples, prepared by spiking a "clean" sea water sample (<0.5 μg-Zn/l), and deionised water with two zinc concentrations in the calibration range (5 and 20 μg-Zn/l). The source of the QC spike was different from that used for calibration.

Figure 1 shows a typical calibration curve, which exhibits a linear response to at least 50 μg/l, with an insignificant blank. A Shewhart control chart (Figure 2) shows all but two of the control samples within the 22 batches of samples analysed (each with two control samples containing 10 μg/l of Zn), were within the 2s control limits. Performance test results (Table I & II) based on 13 batches of analysis, showed that the method was capable of meeting the precision, bias and limit of detection performance criteria required for routine laboratory-based determination of zinc (based on an EQS of 40 μg/l)[12], as stipulated by the U.K. government which are:

- that the standard deviation should be less than 5% or 1.0 μg/l of the determinand concentration whichever was the larger for a concentration range of 0 to 50 μg/l).
- the recoveries for spiked samples (both saline and deionised water) should be between 90–110% of the reference value.
- the limit of detection should be 4 μg/l or better..

Use of the technique in an interlaboratory test of the UK National Marine Analytical Control Scheme gave a result of 9.8 μg L^{-1}, compared with a consensus value from 12 expert laboratories of 10.1 μg L^{-1}, and analysis of a Canadian coastal water standard reference material (CASS-3) gave a result of 1.21+/- 0.11 μg L^{-1} compared with the reference value of 1.24+/- 0.25 μg L^{-1}.

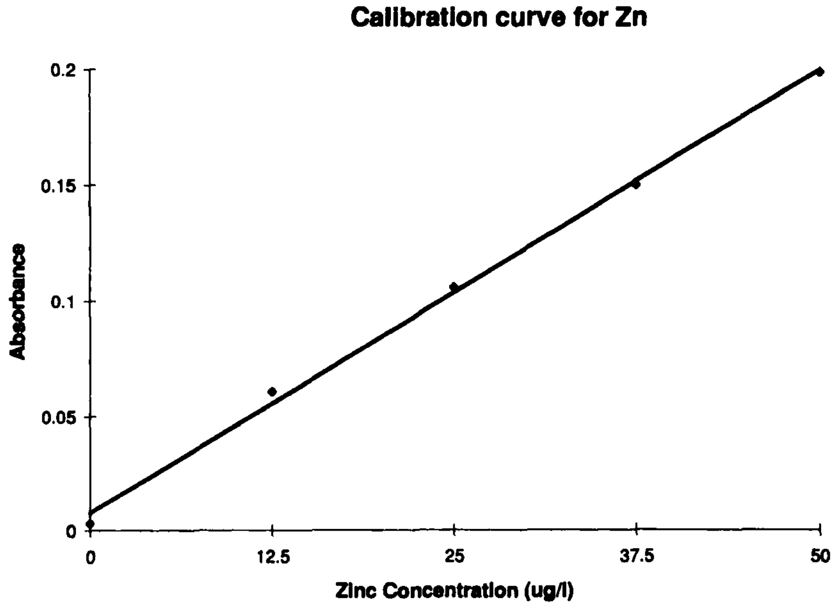

FIGURE 1 Calibration curve for zinc method

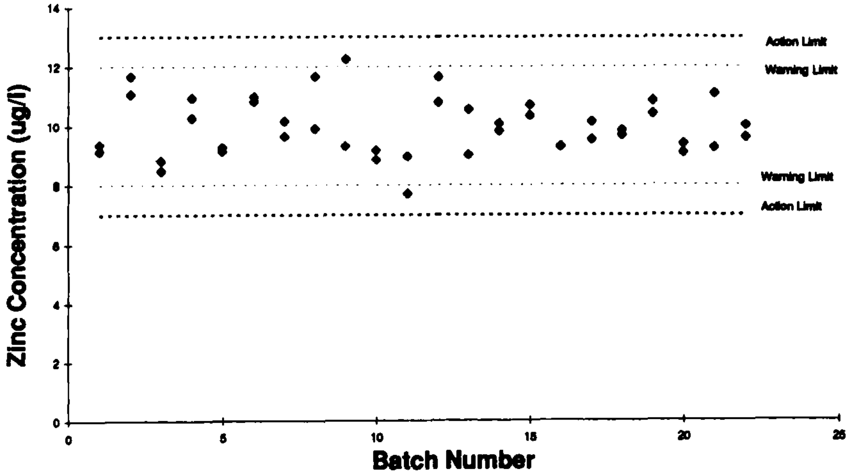

FIGURE 2 Shewhart control chart for 22 batches of routine sample for zinc determination

TABLE I Performance data for the laboratory-based zinc method (13 batches)

BATCH	*Blank*	*Low Standard DIW (5 µg/l)*	*High Standard DIW (20 µg/l)*	*Control Seawater (10 µg/l)*
MEAN	0.56	5.21	19.91	9.84
S_W	0.144	0.216	0.927	0.827
S_B		0.366	0.539	0.358
S_T		0.425	1.072	0.901
DEG F		15	23	24
Assessment with respect to targets		**PASS**	**PASS**	**PASS**
Limit of detection = 0.72 µg/l				

S_W = Within batch standard deviation
S_B = Between batch standard Deviation
$F_{0.05}$ = F-test value ($p=0.05$)
S_T = Total standard deviation
Calc F = calculated F-value based on dataset
M1 = Between batch mean square
DEG F = degrees of freedom
M0 = Within batch mean square
DIW = Deionised water

TABLE II Recovery data for the zinc determinations

	LOW SPIKE	*HIGH SPIKE*
Grand mean recovery (µg/l)	4.65	19.35
s.d. of mean recovery	0.62	0.98
95% conf. limit on Grand mean recovery	+/- 0.306	+/- 0.48
Expected recovery	4.997	19.96
% Recovery	93.1 +/- 6%	97.0 +/- 2.4%

CONCLUSIONS

This complexation/preconcentration procedure is capable of determining dissolved zinc in saline samples to a detection limit of 0.7 µg L^{-1} with an accuracy and precision adequate for the detection of zinc contamination in coastal and estuarine waters. Recoveries of zinc from both deionised water and full saline samples (35 parts per thousand) were 100% (+/- 10%). The technique is simple to use, capable of high volume throughput and utilises chemicals and instrumentation commonly available in most laboratories. It offers a cheap and simple alternative to more complex (and more expensive) analytical techniques such as voltammetry and Inductively Coupled Plasma – Mass Spectrometry. It has been reported that APDC-MIBK extraction can be applied to other elements including copper.[10] With further development, this method may therefore offer laboratories a rapid screening procedure for other elements.

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