Simplified Determination of Cadmium, Lead and Chromium in Estuarine Waters by Flameless Atomic Absorption

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A simplified, sensitive and rapid method for determining low concentrations of cadmium, lead and chromium in estuarine waters is described. To minimize matrix interferences, nitric acid and ammonium nitrate are added for cadmium and lead; nitric acid only is added for chromium. Then 10, 20 or 50 μl of the sample or standard (the amount depending on the sensitivity desired) is injected into a heated graphite atomizer, and specific atomic absorbance is measured. Analyte concentrations are calculated from calibration curves for standard solutions in demineralized water for chromium or an artificial seawater medium for lead and cadmium.

Analytical ranges ($\mu g \, l^{-1}$) with two instruments were linear at 0.1–1.0 and 1.0–10 for cadmium, 4–20 and 10–100 for lead, and 0.2–5 and 5–100 for chromium. Detection limits ($\mu g \, l^{-1}$) were 0.1 for cadmium, 4 for lead and 0.2 for chromium. For cadmium (0.5 and 5 $\mu g \, l^{-1}$), lead (4 and 50 $\mu g \, l^{-1}$) and chromium (1 and 10 $\mu g \, l^{-1}$) in half-strength artificial seawater, the relative standard deviations ($n = 10$) were 20 and 9.5, 18 and 10.4 and 25 and 8.0% respectively.

The proposed method was used to determine cadmium, lead and chromium in 52 estuarine water samples. Cadmium was detected in 11 samples and ranged from 0.5 to 9.7 $\mu g \, l^{-1}$, no lead was detected in any of the samples, and chromium was detected in 5 samples at concentrations from 0.5 to 2.0 $\mu g \, l^{-1}$.

KEY WORDS: Flameless atomic absorption, cadmium, lead, chromium.

INTRODUCTION

Although direct-injection flameless atomic absorption spectrometry is a sensitive tool for determining trace metals, its use with estuarine water presents difficulties because of the nonspecific attenuation and depression

of signal due to salts such as sodium chloride and sodium sulfate.[1-4] Matrix interference for lead and cadmium have been extensively studied.[5-7]

The high background can be overcome by solvent extraction,[8-10] but this technique is time-consuming and error-prone. Segar and Gonzalez[1] attempted to reduce background for a number of metals by a selective volatilization method in which the analyte is volatilized separately from the interfering salts. This technique was not successful for cadmium, lead or chromium. Ammonium nitrate addition has been used to remove chlorides in the form of volatile ammonium chloride during the charring step.[11]

Since matrix interferences cannot be completely eliminated, background correction and compensation for variations of recovery are necessary. A deuterium lamp is commonly used to correct for nonspecific attenuation in the u.v. range.[1,12,13] The standard additions technique, although it has several limitations,[14] has been used to compensate for matrix effects on the specific analyte signal.[1,15-17].

We offer here a alternative to the standard additions method for analysis of estuarine water which combines the advantages of selective volatilization and ammonium nitrate addition with the convenience of direct determination. The key to this new method is calibration with demineralized water for chromium and with an artificial seawater (ASW) medium for cadmium and lead.

EXPERIMENTAL

Apparatus

A Perkin-Elmer heated-graphite atomizer (HGA-2100) equipped with normal (or pyrolytically-coated) tubes was first used in conjunction with a system composed of a monochromator (Jarrell-Ash, Model 82/410), photomultiplier (Pacific Photooptics Instruments, Model 3150), amplifier (Masters Instruments Ltd., Model PT75) and recorder (Envirotech Corp., Model SC-1200R). Sequential background correction was made with a deuterium lamp for lead and cadmium or a quartz-iodine lamp for chromium. Later, a Perkin-Elmer Model 372 atomic absorption spectrophotometer was used with simultaneous deuterium-arc background correction. Hollow cathode lamps were used for all elements. Operating parameters are described in Table I.

Reagents and standards

Reagent-grade chemicals were used throughout. All solutions were prepared with demineralized water containing 10 ml of concentrated (71%)

TABLE I

Instrument conditions

Metal	Wavelength (nm)	Gas flow rate[a] (ml min^{-1})	Drying		Charring		Atomization	
			°C	s	°C	s	°C	s
Lead	283.3	20	110	20	700	20	2200	5
Chromium	357.9	15	110	20	1200	30	2700	5
Cadmium	228.8	15	110	20	300	20	1900	5

[a]Interrupted gas flow used with Perkin-Elmer Model 372 for measurement at the low level

nitric acid per liter (DAW) unless otherwise specified. ASW containing sodium sulfate and chlorides of sodium, magnesium, calcium and potassium was prepared according to the Environmental Protection Agency,[17] except that sodium hydrogen carbonate, potassium bromide, boric acid, strontium chloride and sodium fluoride were omitted. These omissions did not measurably affect the nonspecific attenuation. The ASW solution had a salinity of 36‰.

For each metal a stock solution (1 g l^{-1} as nitrate) was prepared with DAW and stored at 22°C for up to 6 months. Intermediate solutions (1 and 10 mg l^{-1}) were stored at 22°C for up to 1 month.

Standard solutions were prepared weekly with DAW or the appropriate ASW dilution and were stored at 22°C for up to 1 month.

Samples and controls

Fifty-two samples were collected in polyethylene bottles, preserved with nitric acid, pH < 2, and stored at 22°C for up to 60 d. Samples were collected in the New York City area from the Hudson, East and Harlem rivers, Jamaica Bay and Long Island Sound.

To determine the effect of added nitric acid concentrations on the samples, we used five aqueous solutions containing 5.0, 10.0, 20.0, 50.0 or 100 ml of concentrated nitric acid (71%) per liter and 50 ppb each of cadmium, lead and chromium.

Recommended procedure

Determine the salinity of each sample. For lead analysis, dilute the sample to < 18‰ salinity with DAW. In each 100-ml sample to be assayed for lead (diluted or undiluted) or cadmium, dissolve ammonium nitrate as follows: salinity 0–9‰, 7 g; 10–18‰, 15 g; 19–27‰, 24 g; 28–36‰, 30 g.

Calibration

Prepare a set of five standard solutions within each analytical range using

DAW for chromium and the ASW dilution whose salinity is within approximately 5‰ of that of each diluted or undiluted sample for cadmium and lead.

Recovery Study

After the original 52 estuarine water samples were analyzed, 21 of these were spiked and reanalyzed for cadmium and lead and 10 for chromium. Cadmium was added at four concentrations (2, 5, 7.5 and $10 \mu g l^{-1}$) and lead and chromium each at five concentrations (10, 20, 50, 75 and $100 \mu g l^{-1}$).

Recovery was calculated as the ratio of the slope of the regression line obtained with each series of spiked samples to the slope of the corresponding calibration line.

Effect of organics

The effect of glucose, leucine and tryptophan on the response of cadmium, lead and chromium (1, 10, $10 \mu g l^{-1}$) was investigated. Glucose, leucine, and tryptophan in the range of 0.2 to $2 mg ml^{-1}$ was added to DAW and the response compared to that of cadmium, lead and chromium in DAW alone.

RESULTS

Effect of nitric acid concentration

Values for $50\text{-}\mu g l^{-1}$ aqueous solutions of Cr and Pb and $10 \mu g l^{-1}$ for Cd were consistent from 0.1–2% nitric acid.

Nonspecific attenuation

The light attenuation of unspiked ASW dilutions and the relative intensity of the background signal (unspiked vs. spiked solution) for various dilutions of ASW are illustrated in Figure 1. The considerable light attenuation and relative intensity of the background signal at the lead wavelength (at 18‰ absorbance $= 0.220$), combined with the sharp specific signal loss (Figure 2), explain the low precision of lead measurements obtained in ASW diluted to half-strength (Figure 3). This very poor precision for lead at salinities $\geq 18‰$ indicated that direct analysis of lead in undiluted estuarine samples may not be satisfactory.

Although a considerable attenuation occurred at the analytical wavelength of cadmium (Figure 1), precise measurements were possible (Figure 3) even in undiluted ASW because the specific and the intense nonspecific
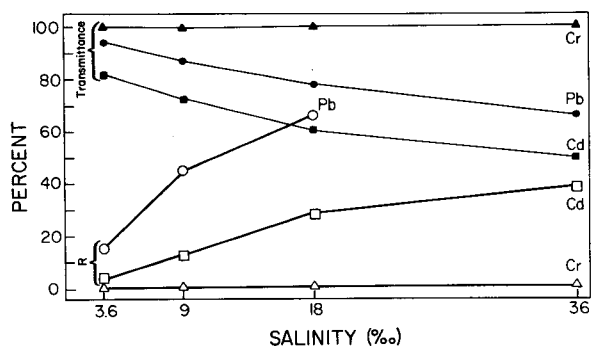
FIGURE 1 Nonspecific attenuation at the specific wavelengths for three metals and the relative intensities (R) of their background signals in various ASW dilutions. Each value of R was calculated as the ratio of background signal in an unspiked solution to that in a spiked solution ($100\,\mu g\,l^{-1}$ for lead or chromium, $10\,\mu g\,l^{-1}$ for cadmium).
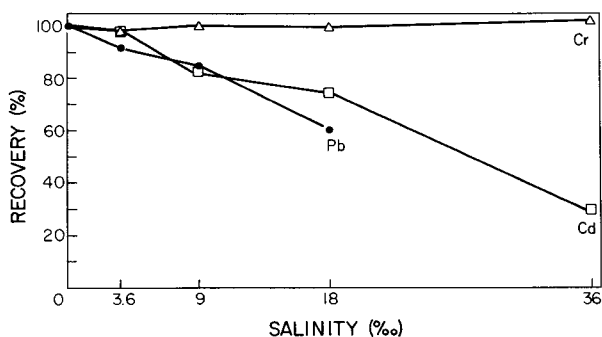

FIGURE 2 Percent recovery of cadmium, lead and chromium in various ASW dilutions relative to aqueous standards. The ASW matrix for chromium did not contain ammonium nitrate.
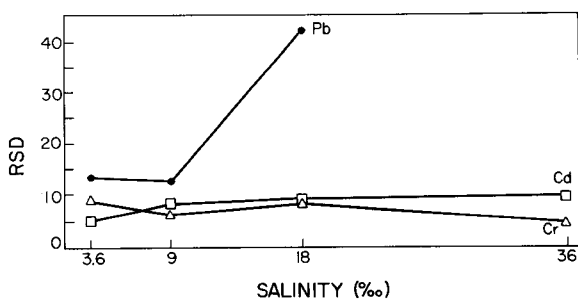

FIGURE 3 Relative standard deviations (RSD) for cadmium ($2\,\mu g\,l^{-1}$), lead $20\,\mu g\,l^{-1}$) and chromium ($10\,\mu g\,l^{-1}$) in various ASW dilutions. For each value, $n=10$.

signals are separated. No background correction was required. A similar effect was observed by Segar and Cantillo.[18]

No background attenuation was observed at the analytical wavelength of chromium even in full-strength ASW with either the deuterium or the quartz-iodine lamp. The absence of a background signal (Figure 1) and the independence of the chromium signal from salinity (Figure 2) explain the observed independence of precision from salinity (Figure 3).

Linear range, precision and detection limits

Calibration curves for standards prepared in undiluted ASW (for cadmium), 50% diluted ASW (for lead), or DAW (for chromium), are linear at 0.1–1 and 1–10, 4–20 and 10–100, and 0.2–5 and 5–100 $\mu g l^{-1}$ respectively. The lower ranges were used with the newer instrument.

Precision was assessed by 10 determinations each of solutions containing 2 μg of cadmium, 20 μg of lead, or 10 μg of chromium per liter (Figure 3) in ASW at each of the four dilutions or in DAW for chromium determinations. For cadmium a moderate increase in relative standard deviation (RSD) from 5.0 to 9.3% with increasing salinity coincides with the corresponding loss of specific signal (Figure 2). For lead the RSD increased sharply as salinity increased from 9 to 18‰. For chromium the RSD varied between 4.5 and 9.0% and appeared independent of salinity within the range investigated.

In a separate experiment at other concentrations the RSDs ($n = 10$) were 9.5% for cadmium (5 $\mu g l^{-1}$) and 10.4% for lead (50 $\mu g l^{-1}$) in halfstrength ASW (salinity 18‰). With the newer instrument and 50 μl of sample, the RSDs ($n = 10$) were 20% for cadmium (0.5 $\mu g l^{-1}$) and 18% for lead (4 $\mu g l^{-1}$). The detection limits, defined as the concentration which gives a mean ($n = 10$) net absorbance ≥ 0.004 with a RSD $\leq 50\%$ at 18‰ salinity, were determined to be (in $\mu g l^{-1}$) 0.1 for cadmium, 4 for lead and 0.2 for chromium.

Analysis of samples

Cadmium was detected in 11 samples, lead in none, and chromium in 5 of the 26 samples analyzed using the newer system. The specific concentrations are reported in Table II. Analyte concentrations ($\mu g l^{-1}$) in the remaining samples tested using the initial system were <2 for cadmium and <10 for lead and chromium.

Recovery study

Recoveries ranged from 87 to 108% for lead, from 91 to 114% for cadmium and from 97 to 104% for chromium with mean recoveries and relative standard deviations of $97.8 \pm 6.5\%$ for lead, $100 \pm 6.8\%$ for

TABLE II

Concentrations ($\mu g\,l^{-1}$) of cadmium and chromium in estuarine water samples[a]

	Cadmium			Chromium	
Sample	Salinity	Concentration	Sample	Salinity	Concentration
17	24.1	2.1	40	23.4	0.5
31	19.4	1.2	E3	23.8	0.9
34	23.8	2.1			
41	25.2	2.1			
H-3	28.8	9.7			
H-8	26.6	4.4			
H-13	18.4	6.2			
K3	24.5	7.4			
5 top	10.0	0.5	5 top	10.0	0.9
5 mid	15.1	3.0	5 mid	15.1	2.0
5 bot	21.2	2.3	5 bot	21.2	2.0

[a]Lead was not detected in any of the 52 samples analyzed.

cadmium and $100\pm2.4\%$ for chromium. There was no difference in response of samples, DAW or ASW when spiked with either hexavalent or trivalent chromium.

Effect of organics

The response for cadmium, lead and chromium (1, 10, $10\,\mu g\,l^{-1}$) was found to be the same in DAW and with or without 0.2 to 2 mg/ml glucose, leucine or tryptophan.

DISCUSSION

The proposed method minimizes the interference effects of the normal components of estuarine waters by adding ammonium nitrate and by using the ASW calibration medium for lead and cadmium. It also has the advantages of reduced analysis time and simplicity of operation. Both rapid and precise, it is especially suited for routine application of estuarine water samples enriched in the metals of interest.

This method is not sufficiently sensitive for the extremely low concentrations of metals reported in unpolluted ocean water.[1, 18, 19] Preconcentration or extraction techniques are required for this purpose.

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