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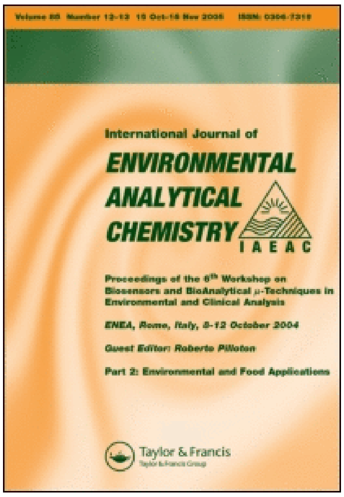

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Optimization of Heating Programs of Gfaas for the Determination of Cd, C_u, N_i and P_b in Sediments Using Sequential Extraction Technique

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OPTIMIZATION OF HEATING PROGRAMS OF GFAAS FOR THE DETERMINATION OF Cd, Cu, Ni AND Pb IN SEDIMENTS USING SEQUENTIAL EXTRACTION TECHNIQUE

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The volatilization behaviors of Cd, Cu, Ni and Pb in different extracting media have been studied using graphite furnace atomic absorption spectrometry (GFAAS) to determine metal concentrations in natural sediments. Considerable interference was found for Cd, Ni, and Pb in the extracts of high matrix concentrations, and could be largely reduced by carefully selecting the ashing and atomization temperatures of GFAAS. Optimal heating programs are proposed to suit a variety of extracts containing different matrices.

KEY WORDS: Metals, sediments, sequential extraction, GFAAS.

INTRODUCTION

Sequential extraction techniques[1,2,3] have been widely used by geochemists to study the distribution of heavy metals in various sedimentary components of sediments. In that technique a sediment sample is treated stepwise with various extracting reagents, and the concentrations of metals extracted from each step are determined by the graphite furnace atomic absorption spectrometry (GFAAS). Since the extracts contain variable amounts of leachable ions, the vaporization behavior of metals in the atomizer may change drastically[4], and thus will influence the precision and accuracy of the analysis. As a consequence, a

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*To whom correspondence should be addressed selection of appropriate ashing and atomization temperatures of GFAAS is of importance for metal determination in the analysis of sediments.

This paper describes the selection of optimum heating programs for the graphite atomizer following the ashing and atomization test of Slavin and Manning.[5] The test can provide an upper temperature threshold for ashing the sample without losing the analyte and a proper atomization temperature for better precision with the least background interference.

MATERIALS AND METHODS

Reagents

Preparation of reagents for the extraction are followed that of Chester et al.[3] except that all reagents were previously purified using either Chelex-100 technique or sub-boiling distillation.[6]

Standards

A series of mixed metal standards were prepared from Merck Titrisol Standards with appropriate dilution.

Extraction procedures

The sequential extraction scheme (Figure 1) used in this study followed the procedures of Tessier et al.[1] with minor modifications by Towner[2] and Chester et al.[3]

Sediment sample

An estuarine sediment was collected at Tanshui River, northern Taiwan. Accurately 0.200g of the dried and homogenized sample was placed in a 50 ml capped polypropylene centrifuge tube and was treated sequentially with different reagents as shown in Figure 1.

Atomic absorption spectrometer

The determination of metals was performed with a Hitachi Zeeman GFAAS (model Z-8100 with an autosampler SSC-200). New graphite cuvettes were combusted at 3000 °C(5 s) several times to eliminate impurities.

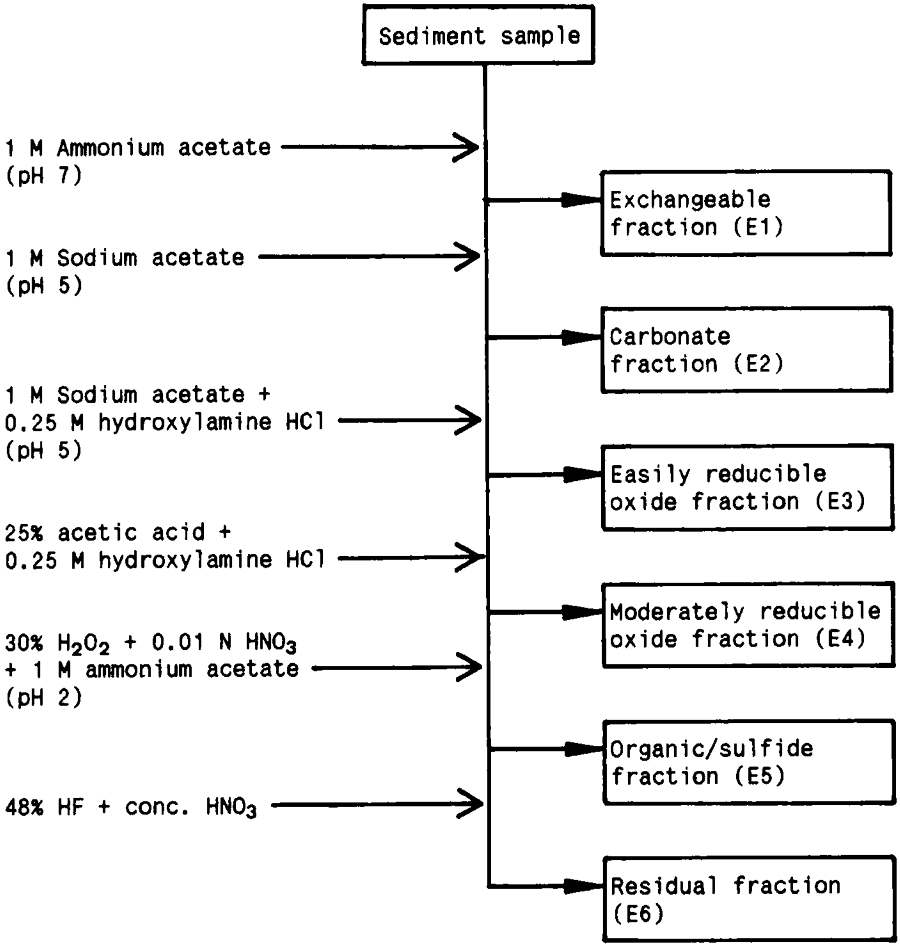

Figure 1 Flow chart showing the sequential extraction scheme (after Chester et al.,[3]) used in this study.

RESULTS AND DISCUSSION

Matrix in extracts

Table 1 lists the major matrices that may present in various extracted fractions. To prevent metals from absorbing onto the vessel wall, all fractions collected were further added with 1%(v/v) conc. nitric acid. As seen in Table 1, the blank extractants(B1-B6) are similar to that of the extracts(E1-E6) except that the latter contain additional soluble substances leached from the sediments.

Table 1 Composition of salt matrix in the extracts during different steps of extraction.

step		*Composition**		
		Blank extractant		*Extracts from a sediment*
1	B1	1M NH_4OAc	E1	1M NH_4OAc + leachable components
2	B2	1M NaOAc	E2	1M NaOAc + leachable components
3	B3	1M NaOAC+0.25M NH_2OHHCl	E3	1M NaOAC+0.25M NH_2OHHCl + leachable components
4	B4	25% HOAc+0.25 M NH_2OHHCl	E4	25% HOAc+0.25 M NH_2OHHCl + leachable components
5	B5	30% H_2O_2#+0.01N HNO_3 +1M NH_4OAc	E5	30% H_2O_2#+0.01N HNO_3 +1M NH_4OAc + leachable components
6	B6	Remains of HF/HNO_3#	E6	Soluble components after HF/HNO_3 digestion

*All fractions were further acidified to 1 % v/v conc. nitric acid to prevent adsorption of metal onto the vessel.

The actual concentrations of H_2O_2 and HF/HNO_3 may vary during the different stage of heating and thus may differ from one batch and another.

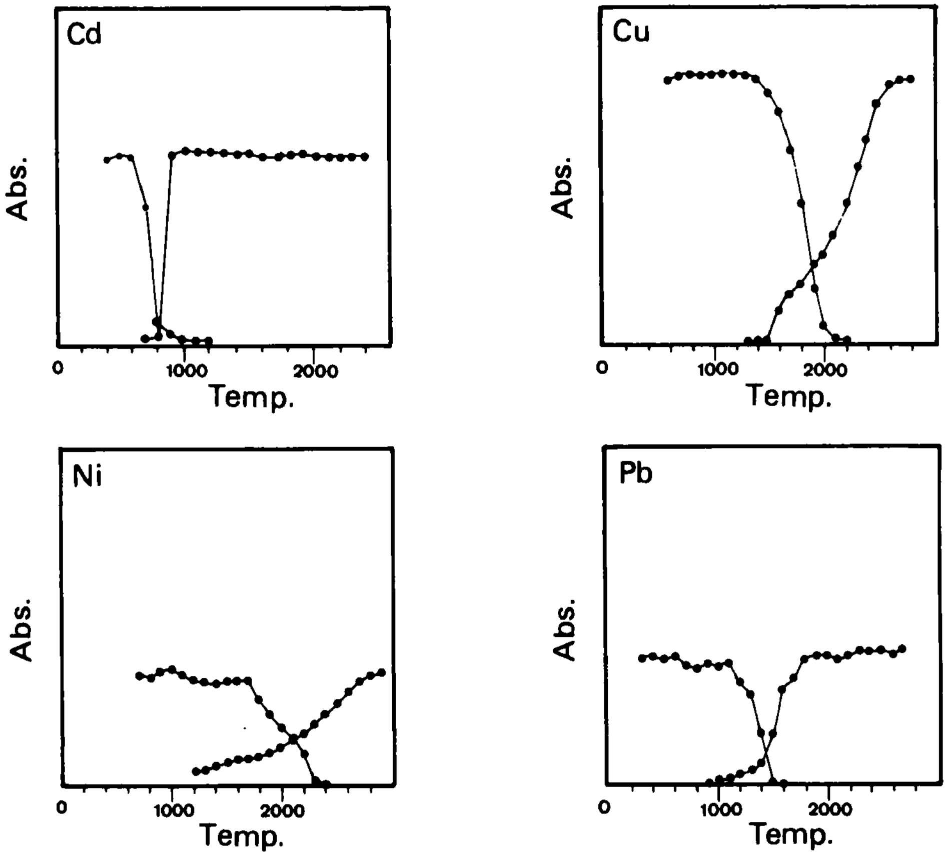

Figure 2 Absorbance vs. ashing and atomization temperature curves for Cd, Cu, Ni and Pb in distilled water medium. Absorbances are in arbitary unit. The distilled water was pretreated with 1 % v/v nitric acid and spiked with Cd, Cu, Ni and Pb of 5, 100, 100 and 50 ng/ml respectively.

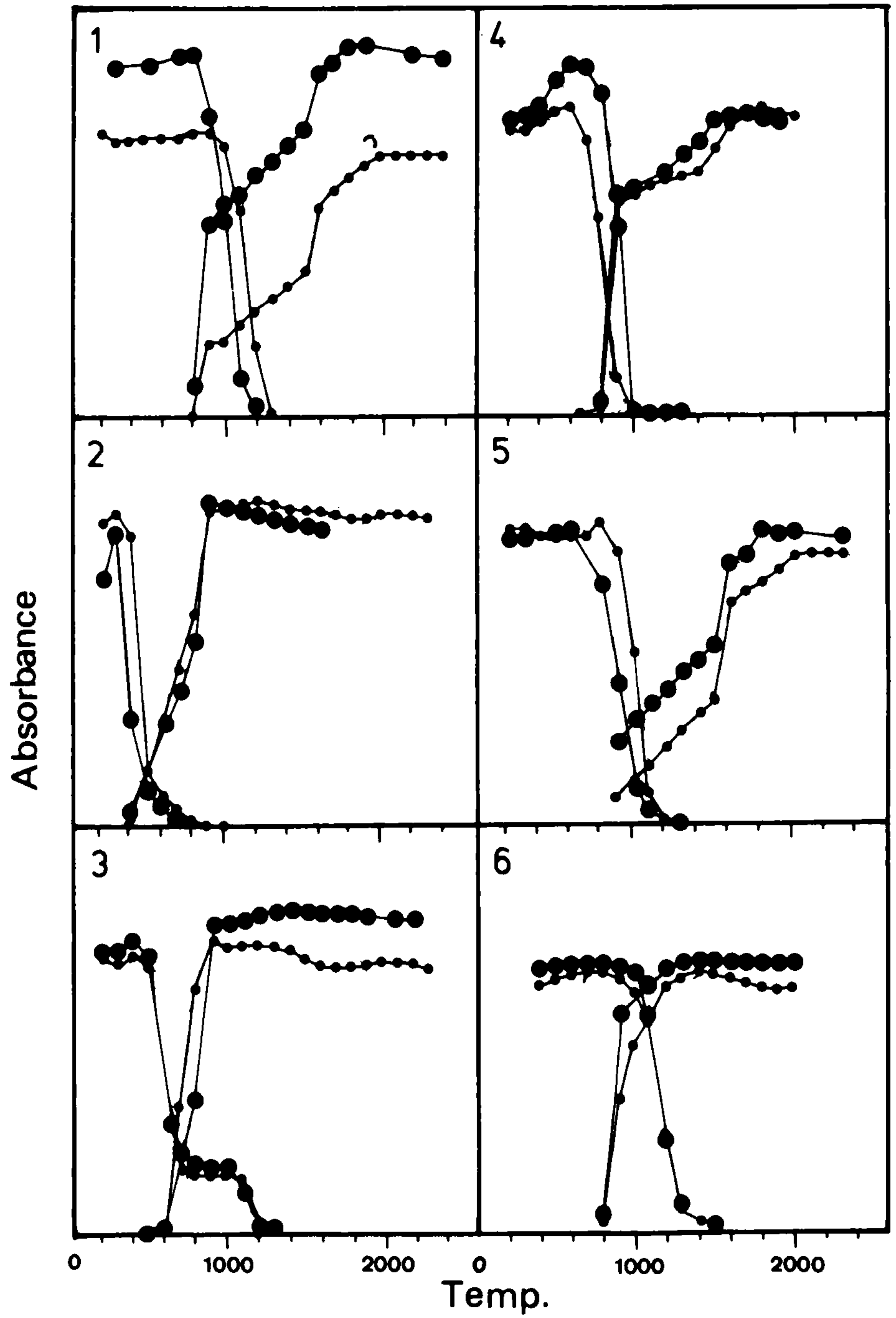

Figure 3 Ashing and atomization plots (left: ashing curve, right: atomization curve) for Cd in the six extracts(all spiked with 5 ng/ml Cd). The arabetic number in the upper left corner denotes extraction stage. Absorbances are in arbitary unit. Small dot: blank extractants(B1-B6). Large dot: sediment extracts(E1-E6).

Ashing and atomization plots

Each of the listed fractions was spiked with known amounts of metals to give concentrations of 5 ng/ml Cd; 100 ng/ml Cu; 100 ng/ml Ni, and 50 ng/ml Pb. During the ashing test, the atomization temperatures were set at 2000, 2700, 2800 and 2000 °C for respective Cd, Cu, Ni, and Pb, while the ashing temperatures were gradually increased from 300 °C with a 100 °C increment. For the atomization test, the ashing temperatures were set at 300, 700, 1200 and 300 °C respectively for Cd, Cu, Ni and Pb, and the atomization temperatures started at 400 °C for Cd and Pb, at 900 °C for Cu and at 1300 °C for Ni, then raised with a 100 °C increment. The resulting absorbances during both tests were plotted as a pair of ashing and atomization curves. Figure 2 shows the plots of the four elements in distilled water medium with addition of 1%(v/v) nitric acid.

Intercept point

The ashing curves intersect the atomization curves at different temperatures. When projected to the temperature axis, the crossing points can be used to indicate the temperature at which analytes roughly lose by half during the ashing stage. The intercept of each pair can further be used to compare the volatilization of metals in different media.

Cadmium

Cadmium is a high volatile element, and is characteristic of less vaporization heat and low appearance temperature in the GFAAS analysis.[4] In the distilled water medium, absorbance of cadmium began to lose at an ashing temperature of greater than 500 °C, while the optimal absorption could be attained at an atomization temperature over 1000 °C (Figure 2). The intersect of the two curves in distilled water medium was at 800 °C. The influence of matrix to the volatilization of Cd has been clearly shown in plots made for different blank extractants which were spiked with equal amount of Cd(Figure 3). In matrices B2 and B3 (incidentally containing high concentrations of Na ions), the appearance temperatures of cadmium are lower than those in distilled water, and the intersect were found to be at 500 and 700 °C. In contrast, in matrices B1, B2, B5 and B6, the temperatures of intersect raised to 1200, 900, 1100 and 1100 °C, respectively.

For extracts (E1-E6) from a natural sediment, the ashing and atomization temperature curves show similar shapes to those of the blank extractants (fractions B1-B6), with intercept temperatures either lower or higher than that obtained in distilled water medium. The shiftings in these temperatures reflect the fact that the volatilization behaviors of Cd change significantly when matrices present, and thus affect the validity of the detection. For example, to detect Cd in fraction E2, the ashing temperature must be set below 300 °C, above which significant loss of metals may occur. However, for

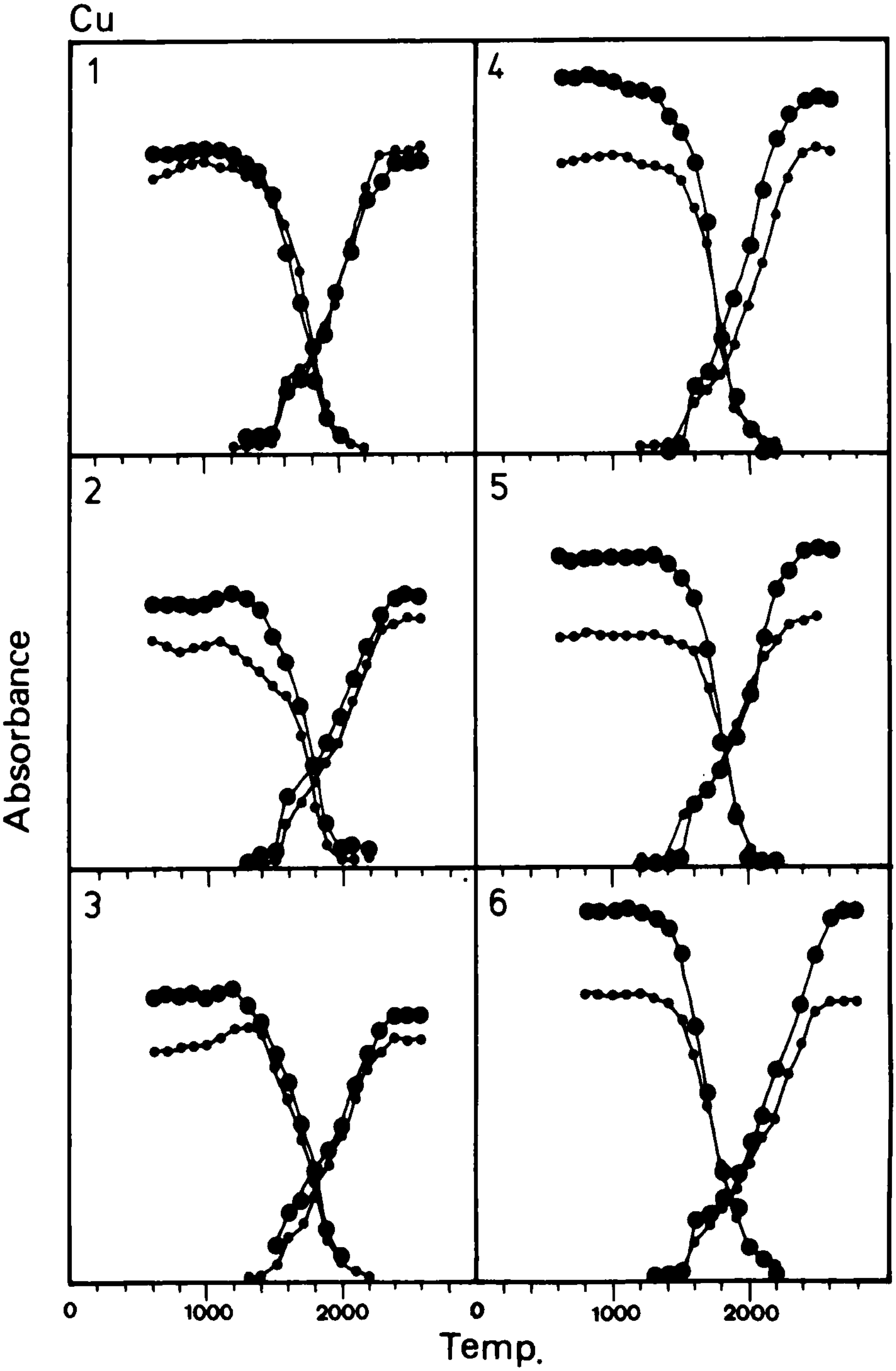

Figure 4 Ashing and atomization curves for Cu in the six extracts(all spiked with 100 ng/ml Cu). Symbols refer to Figure 3.

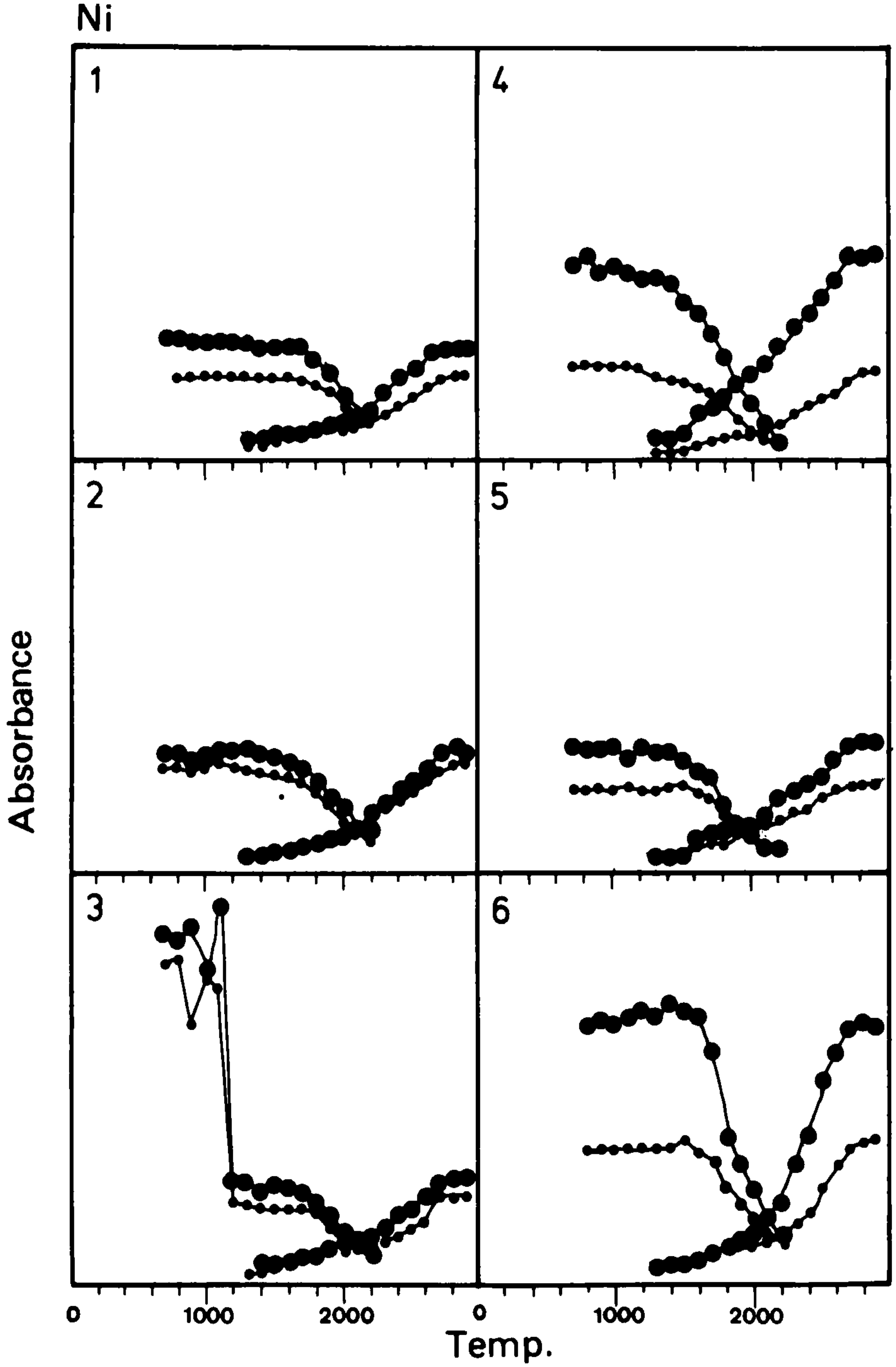

Figure 5 Ashing and atomization curves for Ni in the six extracts(all spiked with 100 ng/ml Ni). Symbols refer to Figure 3.

fraction E5 which contains substantial organic substances, the ashing can be set at a much higher temperature, e.g. 800 °C without loss of Cd. For analyzing Cd in different sediment extracts, the detection can therefore be improved by careful adjustment of the heating program of the graphite furnace.

Copper

Copper is the only element of the four that showed no obvious matrix effect on the ashing and atomization temperature plots. (Figure 4). Copper began to lose at temperatures higher than 1300-1400 °C, and the optimal absorption occurred at 2400 °C or higher. All intersect points for copper appeared at 1800 °C without significant difference. Nonetheless, the sensitivities of Cu determination could vary as much as 10% for different matrices. Quantification must be made by standard spiking to the matrix of the same components so as to eliminate the effect of matrix difference.

Nickel

The vaporization heat of nickel is slightly higher than that of copper. In all cases, nickel started to lose at ashing temperature of 1500 °C, and the maximal absorption requires an atomization at a temperature of as high as 2700 °C(Figure 5). The intersects of the two curves

Table 2 List of temperature settings recommended for the determination of Cd, Cu, Ni and Pb in sediment extracts.

	Cd	*Cu*	*Ni*	*Pb*
Drying stage (ramp 20s,hold 10s)				
	120 °C	120 °C	120 °C	120 °C
Ashing stage (ramp 10s,hold 20s)				
	extracts E1,E4,E5,E6	all extracts	all extracts	extracts E1,E4,E5,E6
	600 °C	1300 °C	1400 °C	600 °C
	extracts E2, E3			extracts E2, E3
	300 °C			300 °C
Atomization stage (hold 10s)				
	extracts E1,E4,E5,E6	all extracts	all extracts	extracts E1,E4,E5,E6
	2000 °C	2500 °C	2700 °C	2000 °C
	extracts E2, E3			extracts E2, E3
	1000 °C			1000 °C
Clean stage (hold 4s)				
	2500 °C	2700 °C	2800 °C	2500 °C

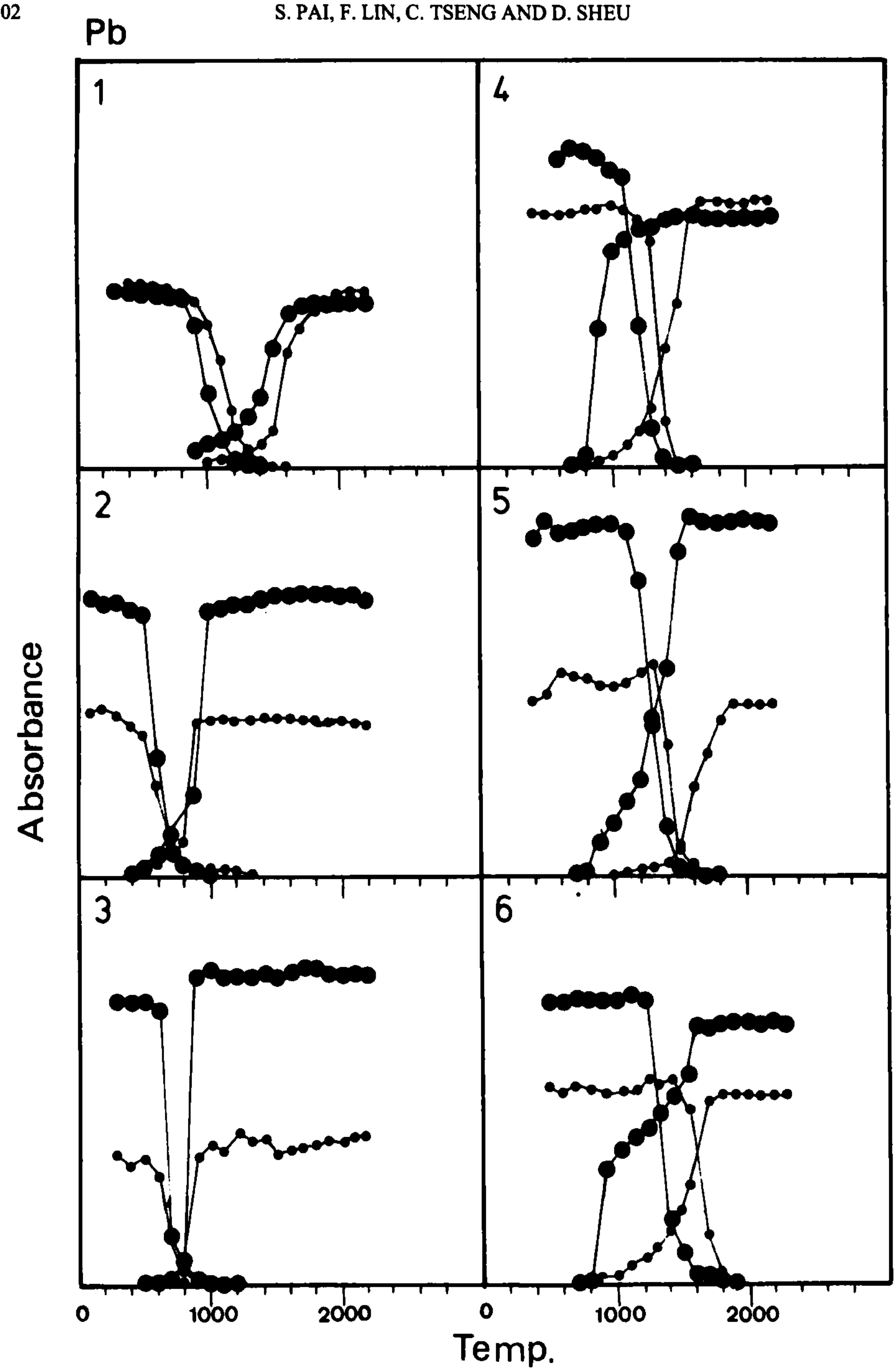

Figure 6 Ashing and atomization curves for Pb in the six extracts(all spiked with 50 ng/ml Pb). Symbols refer to Figure 3.

Table 3 Six-replicate measurements of an estuarine sample by the sequential extraction and detected with GFAAS

extraction step	*Cd (ng/g)*	*Cu (μg/g)*	*Ni (μg/g)*	*Pb (μg/g)*
1	30.6 ± 2.4	0.21 ± 0.02	0.15 ± 0.02	0.43 ± 0.01
2	3.7 ± 0.4	0.58 ± 0.03	2.14 ± 0.19	5.43 ± 0.10
3	1.8 ± 0.3	0.38 ± 0.03	2.22 ± 0.11	3.24 ± 0.20
4	3.2 ± 0.5	3.48 ± 0.32	16.86 ± 1.19	6.15 ± 0.29
5	2.0 ± 0.5	0.24 ± 0.03	4.23 ± 0.15	0.40 ± 0.04
6	2.2 ± 0.6	3.51 ± 0.31	14.80 ± 1.21	3.77 ± 0.35
Sum+sd*	43.5 ± 2.6	8.41 ± 0.45	40.40 ± 1.72	19.43 ± 0.50
Total digestion#	41.1 ± 1.4	8.55 ± 0.30	38.50 ± 1.22	18.35 ± 0.38

* Standard deviation of the added sum was calculated by taking the square root of the summation of the square of each individual standard deviation.

\# Values are concentrations measured by total digestion.

were found at 2100 °C for distilled water, matrices B1, B2, B3, B6 and the corresponding sediment extracts (E1,E2,E3,E6). However, the intersect points for matrices B4, B5 and their extracts(E4, E5) are much lower (1900-2000 °C). The high signals on the ashing curves for B3 and E3 extract at low temperature were observed, which might be caused by the optical interference of NaCl at 232.0 nm.[7] Since the vaporization of NaCl usually occurs at 1200 °C, it is advisable to ash the sample at 1400 °C for at least 20s for nickel determination in order to eliminate the salt interference before atomization.

Lead

Lead is also a comparatively volatile element. In distilled water Pb started to lose at an ashing temperature of 1200 °C, and then reached to a steady absorption at an atomization of 1800 °C. The two curves intersect at 1400 °C (Figure 2) in the distilled water media, but shift to 700 °C in matrices B2, B3 and their corresponding extracts (Figure 6).

It was observed, however, that the vaporization behaviors of Pb in sediment extracts(E1-E6) differs from those in corresponding blank extractants. A steady absorption for the latter was found at atomization temperatures of 1600-1800 °C, while the atomization threshold in sediment extracts was lowered by 200-400 °C, i.e. at 1200-1600 °C. Because of such unpredictable changes, the detection of Pb in different media requires wider temperature thresholds during ashing and atomization.

Recommended temperature program

A series of temperature programs for routine GFASS analysis of heavy metals in sequential extracts are proposed in this study (Table 2). Selection of the temperature thresholds were made with: (1) the ashing temperature of at least 100-200 °C lower than the appearance temperatures of the element, and (2) the atomization temperature of approximately 100 - 200 °C above the minimum threshold. Furthermore, the recommended temperature settings

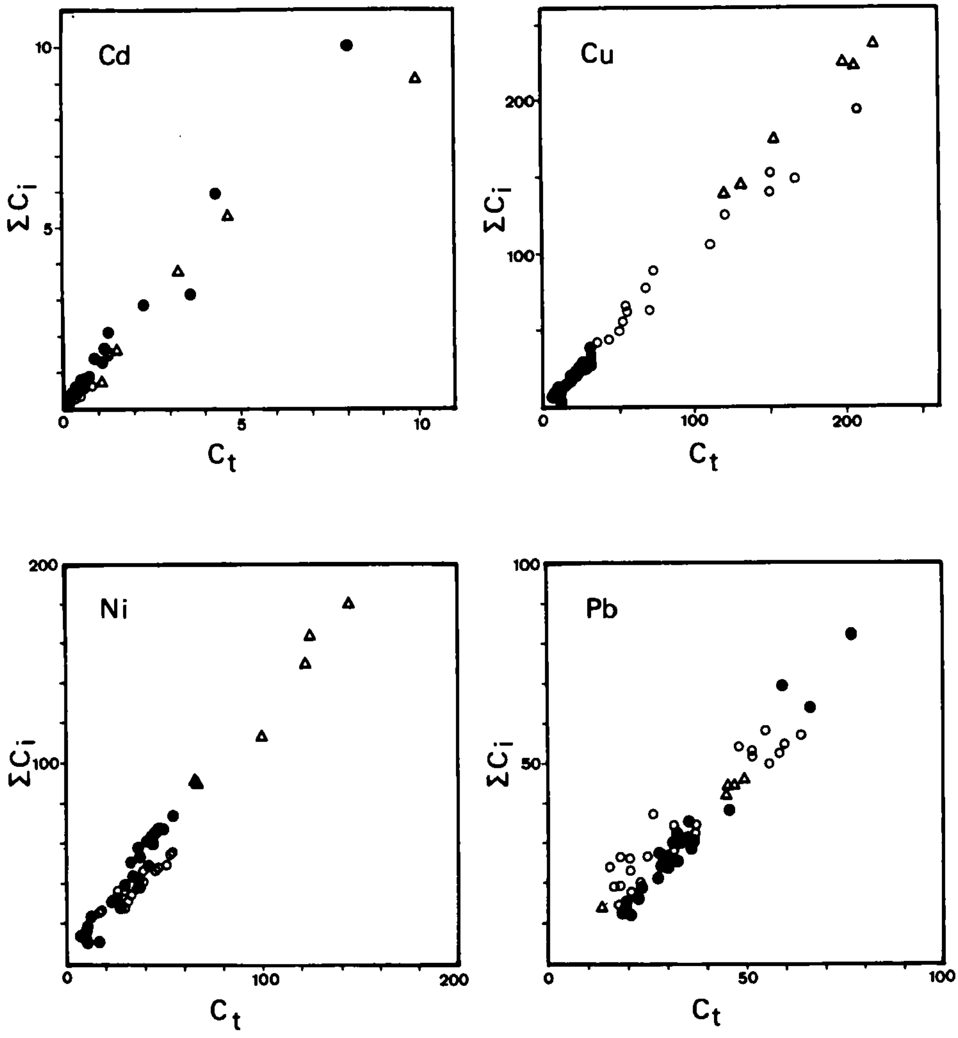

Figure 7 Correlation of the sum of individual metal concentration (in μg/g) measured in different sequential extracts(ΣCi) with the total concentrations of metals in sediments (in$_{\text{Ct}}$, μg/g) (circle: estuarine sediments, dot: shelf sediments, triangle: deep sea sediments).

shown in Table 2 are valid only for cuvettes used in this study. The settings may vary with other types of graphite cuvettes used.

Quantification

During the experiments all matrices were spiked with equal amount of analyte(e.g. 5 ng/ml Cd, 100 ng/ml Cu, etc.). From Figures 2 to 6 it is apparent that the sensitivity of the metal detection in different media varies appreciably, and thus may lead to erroneous results when the concentrations are estimated by one single calibration curve. Although such errors can be largely removed hypothetically by having each extract its own calibration curve, it is not advisable in practice because of the tedious work involved. Additionally, the analyst usually does not know the concentration range prior to the determination. As a consequence, it is suggestive to have a series of known standards adding or spiking to the corresponding extracts from a typical sediment (for example, a reference material). Although some errors may still be existed owing to the slight difference in the matrices, but the error is usually thought to be small and can be neglected.

Data quality

One of the major concerns for analyzing sediment samples is to ensure the data to meet required levels of precision and accuracy. The precision of the technique was demonstrated on analyzing an esturine sediment sample using the proposed temperature settings and the results are shown in Table 3. As can be seen results from the total digestion agree well with the sum from sequential extraction analysis. Furthermore, we have analysed three types of sediments. i.e. 29 riverine/estuarine samples from Tanshui River, Taiwan, 28 shelf sediments from the East China Sea near Taiwan, and 6 deep sea sediments from the Philippine Sea. Results of these studies are plotted in Figure 7. In general, a very good agreement existed between the metal concentrations derived from the total digestion and those summed from the sequential extraction analysis.

CONCLUSIONS

The salt matrix in sediment extracts has been the major concern for the precise and accurate measurement of metal concentrations using GFAAS. The interference of the presence of the salts can be shown by the ashing and atomization test. The choosing of a proper temperature program to better accommodate the vaporization characteristics of a metal in a particular medium would give rise to a better precision and high accuracy during metal analysis.

Cadmium and lead are of comparatively volatile nature, and their vaporization heat change drastically in different media. As a result, cautions need be taken for selecting the temperature thresholds for these two elements. As for the other two less volatile elements, nickel and copper, the ashing temperatures must be set at as high as 1200 or 1400 °C to reduce most of the salt effect before analyzing the metal at the atomization stage.

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