

Cooperative Study of Precision and Accuracy on the Determinations of Around-ppb Levels of Copper and Lead in Environmental Waters

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The results of a series of inter-laboratory cross-check on the determinations of ppb and sub-ppb levels of copper and lead in environmental samples are described. Thirteen laboratories participated during a five-stage comparison. Seven analytical methods and two pre-concentration procedures were performed on certified and real samples. For controlled and blind standards at higher concentration levels (10 ppb or above) the data reported by different participants show good agreement for both elements regardless of the method chosen. However, for samples having lower concentrations (1-10 ppb level), the relative standard deviation (R.S.D.) and bias increased. A high degree of scattering on data were demonstrated for a deep ocean water at less than 1 ppb level. The results of the present study give direct comparison between different analytical methods, and also reflect the average aptitude of analytical laboratories in Taiwan on the measurements of copper and lead in environmental samples.

INTRODUCTION

The discharge of heavy metals from industrial sewage into coastal area surrounding Taiwan has already caused many serious pollution problems in recent years. In order to identify the sources of pollutants and to evaluate their impacts to the natural environment, several intensive monitoring programs have been implemented. Large numbers of samples including waste water, river water, coastal and ocean water are being analyzed on a routine basis in many laboratories. A question is raised: "How can we be sure that those data reported by different laboratories are correct, meaningful, and compatible with each other"? In a previous study¹ it has been found that at ppm or above levels the data reported by different laboratories accorded well even using different methods. This indicates that the monitoring work at high (ppm) level is not a difficult task to most laboratories with present-day chemicals and instruments. However, if

the target range drops to ppb levels or less, problems may occur, and the quality of data may vary significantly from one laboratory to another. The following difficulties can be expected: (1) contamination in the sampling process, (2) impurities introduced from the air, water, reagents, labware, and in the analytical processes, and (3) interference caused by the complex matrix in the environmental samples, e.g. waste water or seawater. The third difficulty may be reduced using a separation or pre-concentration procedure, but the former two are hard to control in practice nor can it be identified directly. For these reasons, the frequent inter-laboratory comparison on known or blind samples, although may not eliminate entirely the problems, gives a good indication on the data quality in those large scale monitoring programs.

In this paper we reported the results of a series of inter-laboratory cross-check on the determinations of Cu and Pb in a variety of samples covering freshwater, waste water and

seawater. Thirteen laboratories from nine institutions were participated. The study was conducted in five stages for samples with an increasing complexity (matrix) and a decreasing trend on the concentration level:

Stage 1. Analysis of controlled standards at 10^1 ppb level.

Stage 2. Analysis of blind samples at 10^1 ppb level.

Stage 3. Analysis of reference materials at 10^{-1} - 10^3 ppb level.

Stage 4. Analysis of tap, spring, river, and waste waters at 10^{-1} - 10^2 ppb level.

Stage 5. Analysis of a deep seawater at less than 10^{-1} ppb level.

The methods and instruments applied in this program are listed in Table 1, with abbreviations in brackets.

MATERIALS AND METHODS

Control standard: Two stock standards of 10.0 ± 0.1 ppm of Cu and Pb were prepared in bulk by dissolving 1 g of the metals in conc. nitric acid and diluting them with distilled water. The solutions were prepared at National Tsinghua University and distributed in portions to the participated laboratories. These standards were requested to be diluted 200-1000 folds with distilled water, and then measured against the standards prepared by each laboratory.

Blind samples: Three solutions namely A, B, and C containing known amount of copper and lead (at 10-20 ppb levels) were prepared in bulk at National Tsinghua University and distributed in 1-L polypropylene (PP) bottles. The participants were requested to report the measured concentrations of Pb and Cu in those blind samples. The calibration curves were made from the previous control standards.

Tap water, spring water, river water: Samples were prepared at National Taiwan University after being filtered through a Millipore membrane filter, acidified to 0.1 N with respect to nitric acid, and distributed in 1-L PP bottles.

Waste water: Two waste water samples were prepared by the China Steel Corporation. They were filtered and acidified.

Reference materials: The following commercially available standard reference materials (SRM) were purchased and used in this study: SRM1643C (reference river water), APG (reference waste water), and NASS-2 (reference seawater, purchased from National Bureau of Standards, Ottawa, Canada). Average concentrations of Cu and Pb in these materials were certified by the manufacturers.

Natural seawater: A 1000-m deep seawater sample was collected by the research vessel R/V Ocean Researcher I

Table 1. Methods and Instrumentation (with abbreviations) Involved in This Study

Solvent extraction (SVX)
Chelating ion-exchange (CIX)
Flame absorption spectrometry (AAS)
Graphite furnace absorption spectrometry (GFAAS)
Anodic stripping voltammetry (ASV)
Inductively coupled plasma optical emission spectrometry (ICP-OES)
Inductively coupled plasma mass spectrometry (ICP-MS)
Reverse-phase liquid chromatography (RPLC)
Flow injection analysis (FIA)
2,2'-Biquinoline method (BQ)

during Cruise 316B (May 19-22, 1992). The sampling location was $19^\circ 44.9' N$, $120^\circ 42.9' E$ in the Luzon Channel. The GoFlo bottles (2.5 L, type #1080, General Oceanic Inc. Miami, FL, USA) were used for the sampling and they were all Teflon coated.² Upon retrieving the sampler, seawater was directly filled into 1-L PP bottles each filled previously with 10 mL of sub-boiling distilled nitric acid. After returning from the cruise, these bottles were dispatched immediately to the ten participated laboratories for further measurement.

Data reporting: All participated laboratories were requested to carry out three independent analyses of copper and lead in each sample, and to report their mean concentration values together with three raw data. The purpose of the cross-check analysis is to find out a most probable concentration of the target element in a given sample from the set of the mean values reported by each participant. Since a set of average values also follows normal distribution law, one may use the total average value and its standard deviation to give a measure of how disperse the data values are from the mean. It is therefore not the purpose of the present study to evaluate the quality of the data reported from individual laboratory if any significant dispersion were found, nor to evaluate the ability of any analytical method.

RESULTS AND DISCUSSION

The cross-check on control standards

A series of diluted control standards (range between 10-50 ppb) was determined for Cu and Pb by different laboratories. Five out of nine laboratories chose GFAAS, others used ICP-MS, AAS, FIA-ASV, and RPLC. From the reported results (Table 2) it can be seen that all laboratories provided quite good precision on both elements regardless of the method chosen. Only 4 out of 31 (15 sets for Cd and 16 sets for Pb) reported relative standard deviations (R.S.D.)

Table 2. Analysis of Cu and Pb in Self-Diluted Control Standards

Element	Designated conc. (ppb)	Method used	Lab code	Conc. (ppb) found		Bias (%)	
				Mean \pm S.D.	RSD (%)		
Cu	10	GFAAS	L-6	10.2 \pm 0.2	2	+2	
	20	FIA-ASV	L-9	19.5 \pm 0.7	4	-3	
	20	GFAAS	L-3	19.5 \pm 1.2	6	-3	
	20	GFAAS	L-4	19.7 \pm 0.2	1	-2	
	20	GFAAS	L-5	20.3 \pm 0.7	3	+2	
	20	GFAAS	L-6	20.1 \pm 0.7	4	+0.5	
			Average	19.8 \pm 0.4	2	-2	
	30	AAS	L-7	30.2 \pm 0.6	2	+1	
	30	GFAAS	L-3	28.9 \pm 1.5	5	-4	
	30	GFAAS	L-6	31.1 \pm 0.4	1	+4	
			Average	30.1 \pm 1.1	4	+1	
	32	ICP-MASS	L-1	31.3 \pm 1.1	4	-2	
	40	GFAAS	L-6	38.3 \pm 0.9	2	-4	
	50	GFAAS	L-2	49.9 \pm 0.1	0.2	-0.2	
	50	GFAAS	L-3	48.8 \pm 1.3	3	-2	
	50	GFAAS	L-6	49.5 \pm 3.7	8	-1	
	50	RPLC	L-8	52.7 \pm 1.0	2	+5	
			Average	50.2 \pm 1.7	3	+4	
	Pb	10	GFAAS	L-6	10.1 \pm 0.3	3	+1
		10	GFAAS	L-3	9.3 \pm 1.2	13	-7
			Average	9.7 \pm 0.6	3	+9	
14		FIA-ASV	L-9	15.2 \pm 0.4	3	+9	
20		GFAAS	L-6	20.5 \pm 0.3	2	+3	
20		GFAAS	L-3	20.3 \pm 1.5	7	+2	
20		GFAAS	L-4	21.0 \pm 0.4	2	+5	
			Average	20.8 \pm 0.4	2	+4	
30		GFAAS	L-3	31.0 \pm 1.0	3	+3	
30		GFAAS	L-6	30.6 \pm 0.9	3	+2	
			Average	30.8 \pm 0.3	1	+3	
32		ICP-MS	L-1	32.7 \pm 1.7	5	+2	
40		AAS	L-7	38.0 \pm 1.2	3	-5	
40		GFAAS	L-6	40.6 \pm 0.2	0.5	-2	
40		GFAAS	L-5	40.9 \pm 0.7	2	+2	
			Average	39.8 \pm 1.6	4	-1	
50		GFAAS	L-2	47.7 \pm 1.5	3	-5	
50		GFAAS	L-3	49.1 \pm 1.2	2	-2	
50		GFAAS	L-6	51.0 \pm 1.0	2	+2	
50		RPLC	L-8	52.3 \pm 1.2	2	+5	
		Average	50.0 \pm 2.0	4	0		

larger than 5%. The accuracy was also satisfactory judging from the bias (%) of the data, only 3 out of 31 exceeded 5%. For most environmental work at the ultra-micro level, it is customarily to set $\pm 25\%$ as the acceptable thresholds for both precision and accuracy. The results in Table 2 are far better than these thresholds, and therefore all participants were qualified for proceeding to the next stage of cross-

checking on the blind standards.

Analysis of blind samples

Three blind samples (A, B, and C) were analyzed by ten laboratories using six different methods. Sample A contained 20 ppb Cu only, Sample B contained 20 ppb Pb only; whereas Sample C contained 10 ppb each of Cu and Pb.

Table 3. Analysis of Cu and Pb in Blind Samples (with designated concentrations)

Element	Sample (conc.)	Methods	Lab code	Conc. (ppb) found		Bias (%)	
				Mean \pm S.D.	RSD (%)		
Cu	A (20ppb)	ICP-MS	L-1	20.6 \pm 0.2	1	+3	
		GFAAS	L-2	21.1 \pm 0.5	2	+6	
		GFAAS	L-3	21.0 \pm 1.6	8	+5	
		GFAAS	L-4	20.8 \pm 0.2	1	+4	
		GFAAS	L-5	20.2 \pm 0.1	0.5	+1	
		GFAAS	L-6	19.6 \pm 0.3	2	-2	
		AAS	L-7	20.3 \pm 0.7	3	+2	
		RPLC	L-8	19.7 \pm 0.1	0.5	-2	
		FIA-ASV	L-9	20.9 \pm 0.8	4	+5	
		BQ	L-10	(25)*			
			Average	20.5 \pm 0.6	3	+3	
		C (10ppb)	ICP-MS	L-1	10.3 \pm 0.2	2	+3
	GFAAS		L-2	10.7 \pm 0.1	1	+7	
	GFAAS		L-3	9.0 \pm 0.1	1	-10	
	GFAAS		L-4	10.7 \pm 0.2	2	+7	
	GFAAS		L-5	10.4 \pm 0.1	1	+4	
	GFAAS		L-6	10.2 \pm 0.6	6	+2	
	AAS		L-7	10.8 \pm 0.5	5	+8	
	RPLC		L-8	10.7 \pm 0.2	2	+7	
	FIA-ASV		L-9	10.6 \pm 0.5	5	+6	
BQ	L-10		(10)*				
		Average	10.4 \pm 0.6	5	+4		
Pb	B (20ppb)	ICP-MS	L-1	19.4 \pm 0.4	2	-3	
		GFAAS	L-2	17.3 \pm 0.1	1	-14	
		GFAAS	L-3	19.9 \pm 0.6	3	-0.5	
		GFAAS	L-4	21.6 \pm 0.3	1	+8	
		GFAAS	L-5	21.1 \pm 0.5	2	+6	
		GFAAS	L-6	21.4 \pm 0.4	2	+7	
		AAS	L-7	20.7 \pm 0.3	1	+4	
		RPLC	L-8	19.1 \pm 0.3	2	-5	
		FIA-ASV	L-9	19.2 \pm 1.2	6	-4	
				Average	20.0 \pm 1.4	7	0
		C (10ppb)	ICP-MS	L-1	10.1 \pm 0.2	2	+1
	GFAAS		L-2	8.6 \pm 0.2	2	-14	
	GFAAS		L-3	10.6 \pm 0.2	2	+6	
	GFAAS		L-4	11.2 \pm 0.1	1	12	
	GFAAS		L-5	10.0 \pm 0.2	2	0	
	GFAAS		L-6	10.4 \pm 0.2	2	+4	
	AAS		L-7	9.2 \pm 0.3	3	-8	
	RPLC		L-8	9.4 \pm 0.1	1	-6	
	FIA-ASV		L-9	9.7 \pm 0.6	6	-3	
				Average	9.9 \pm 0.8	8	-1

*Data obtained by the semi-quantitative method (BQ) were excluded in the calculation of the average.

These concentrations were unknown to the participants before the results were sent back.

In general, the precision for both copper and lead measurements (Table 3) of each laboratory was not much different from that in the self-dilution analysis. The reported R.S.D. values were mostly less than 5% with several individual exceptions. Among those methods, the one using the 2,2'-biquinoline (BQ)³ was a semi-quantitative analysis

for copper, therefore the value reported by this method was excluded in the calculation of the total average value.

The R.S.D. of 3 and 5%, respectively, of the two sets of data on 20- and 10-ppb Cu were rather close to the largest R.S.D. values reported by the individual laboratories. In the case of Pb, R.S.D. of 7% of 20-ppb data set and 8% of 10-ppb data set were all larger than the individual ones in the respective set. Furthermore, there is a wider-spreading ten-

dependency on the data distribution (Table 3 and Fig. 1) if compared with that of the self-dilution test on the same concentration level (Table 2). Such tendencies are generally experienced for the blind test.¹ However, all of these R.S.D. values were far better than the desired 25% threshold, therefore, these results may be regarded as very satisfactory.

As to accuracy, both copper and lead analyses showed bias less than 5%, and in the case of 20.0-ppb in Sample B a bias of even coincidentally 0% was found. These results are again far better than the 25%-threshold, and it appears that, at 10-20 ppb level, increasing laboratory number gives a closer value to the true concentration, so far as pure, simple aqueous solutions are concerned.

Analysis of reference materials

Three certified reference materials were used in this stage of cross-check, namely, the APG standard waste water, the SRM1643C standard river water, and the NASS-2 standard seawater. The metal concentrations in the APG-std are comparatively high (113.7 ppb Cu and 1056.5 ppb Pb), and it was measured by four laboratories using direct ICP/OES.

The SRM1643C which contains Cu and Pb at intermediate levels was measured by three laboratories using direct GFAAS. For NASS-2 at the extremely-low concentrations (with 0.109 ppb Cu, and with non-detectable Pb) analysis was made by two laboratories using different methods (ASV and CIX-GFAAS). All results are given in Table 4 and further illustrated in Fig. 1.

The average value of Cu in the APG-std reported by the four participants was 111 ± 12 ppb with a bias of -2% from the certified value. The result for Pb was 1089 ± 32 ppb, corresponding to a bias of +3%. The precision was quite good (R.S.D. = 3%) for lead, but it was less satisfactory for Cu (R.S.D. = 11%).

Three laboratories continued to measure Cu and Pb in SRM 1643C standard using direct GFAAS. The material contained 22.3 ppb Cu and 35.3 ppb Pb as certified by the manufacturer. The average of the reported values were 22.9 ± 0.2 ppb Cu and 32.1 ± 0.8 ppb Pb, both in good agreement with the certified values. The R.S.D. of the respective data set were within 3% for both elements. In general, both the precision and the accuracy were within +10%, far better than the desired 25% thresholds so far as the analyses of Cu and Pb in the controlled and reference standard solutions are

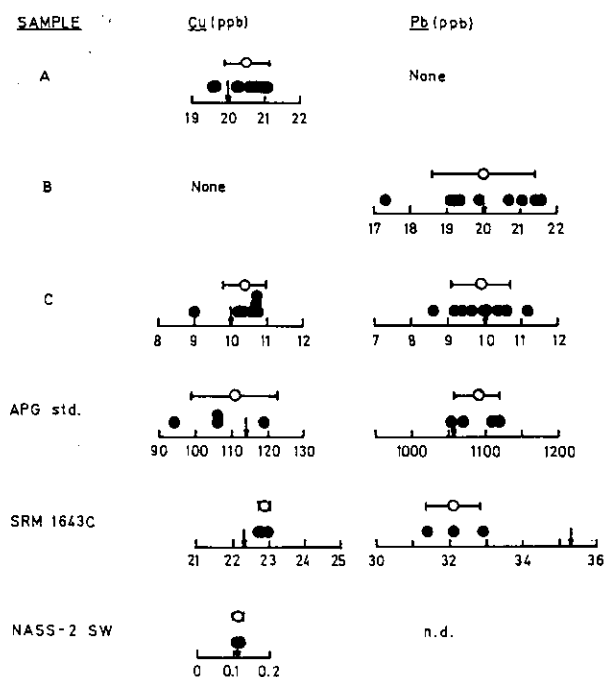


Fig. 1. Individually reported (black points) and average values (circles) of Cu and Pb measurements for the blind samples (A,B,C), and standard reference materials (APG-std, SRM1643C, and NASS-2). Arrows indicate the designated or certified values, and the error bars show the estimated standard deviations. Data are from Tables 3 and 4.

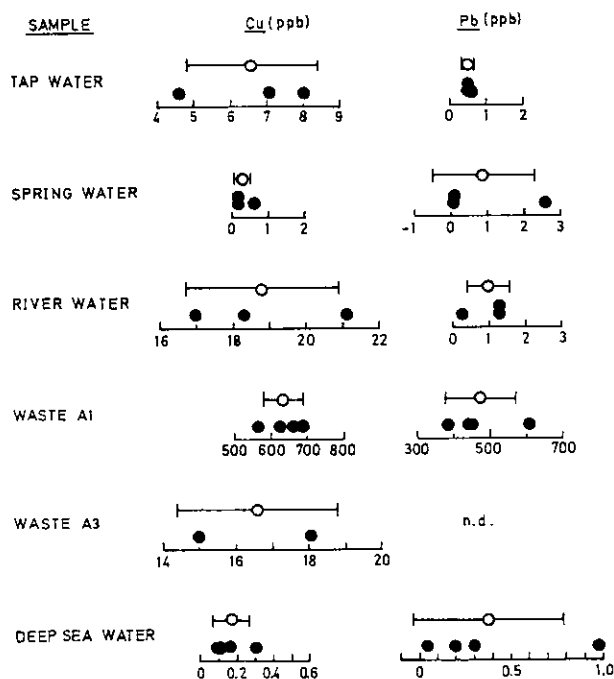


Fig. 2. Individually reported (black points) and average values (circles) of Cu and Pb measurements for the tap water, spring water, waste water, and seawater. For seawater the data obtained without using pre-concentration are not plotted. Data are from Tables 5 and 6.

Table 4. Analysis of Cu and Pb in Certified Reference Materials

Element	Sample	Certified Conc. (ppb)	Method	Lab code	Conc. (ppb) found	Average value (ppb)		Bias (%)
						Mean \pm S.D.	RSD (%)	
Cu	APG-std	113.7	ICP-OES	L-3	119	111 \pm 12	11	+2
			ICP-OES	L-12	116			
			ICP-OES	L-13	94			
			ICP-OES	L-14	116			
	SRM1643C	22.3	GFAAS	L-3	22.7	22.9 \pm 0.2	1	+3
			GFAAS	L-12	22.9			
			GFAAS	L-13	23.0			
NASS-2	0.109	CIX-GFAAS	L-3	0.12 \pm 0.01*	0.115 \pm 0.007	6	+6	
		ASV	L-12	0.11 \pm 0.04*				
Pb	APG-std	1056.5	ICP-OES	L-3	1054	1089 \pm 32	3	+3
			ICP-OES	L-12	1069			
			ICP-OES	L-13	1112			
			ICP-OES	L-14	1120			
	SRM1643C	35.3	GFAAS	L-3	32.9	32.1 \pm 0.8	2	-9
			GFAAS	L-12	32.1			
			GFAAS	L-13	31.4			

* triplicated measurement

concerned as depicted in Fig. 3 and 4.

The NASS-2 seawater was measured by two laboratories, and only Cu was reported. The mean values obtained by the two laboratories were 0.115 ± 0.007 ppb (R.S.D. = 6%), with bias not larger than 6%. At this extremely low concentration, such a result was excellent.

Analysis of tap, river and waste water

The determinations of Cu and Pb in five real samples

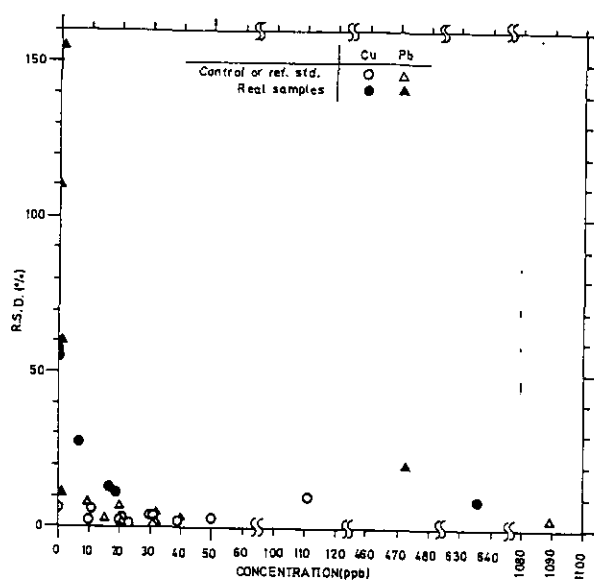


Fig. 3. Diagram showing the relationship between R.S.D. and concentration. Data are from Tables 2-6.

were compared in this stage. The actual concentrations in these samples were unknown, therefore the data reported could only give an average of the measured value rather than an estimate on the accuracy, unless the reproducibility within and between each laboratory can be proven, i.e., R.S.D. of a given data set is within the desired range, and all of the data are reasonably acceptable. The purpose of this comparison was aimed to see how disperse the data sets were at different concentration levels.

Three natural water samples (a tap water, a spring water, and a river water) were analyzed by three laboratories using direct GFAAS. The reported concentrations (Table 5) for Cu were 6.6 ± 1.8 ppb; 0.3 ± 0.2 ppb; and 18.8 ± 2.1 ppb

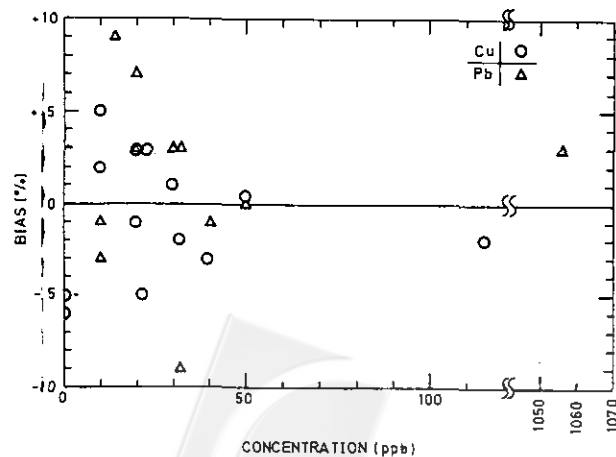


Fig. 4. The relationship of bias and concentration. Data are from Tables 2-4.

Table 5. Analysis of Cu and Pb in Tap, Spring, River, and Waste Waters

Element	Sample	Methods	Lab code	Concentration found (ppb)	Average value (ppb)	
					Mean \pm S.D.	RSD (%)
Cu	Tap water	GFAAS	L-3	7.1	6.6 \pm 1.8	27
		GFAAS	L-12	8.0		
		GFAAS	L-13	4.6		
	Spring water	GFAAS	L-3	0.6	0.3 \pm 0.2	69
		GFAAS	L-12	0.2		
		GFAAS	L-13	0.2		
	River water	GFAAS	L-3	18.3	18.8 \pm 2.1	11
		GFAAS	L-12	17.0		
		GFAAS	L-13	21.1		
	Waste A1	ICP-OES	L-3	692	636 \pm 55	9
		ICP-OES	L-12	565		
		ICP-OES	L-13	623		
		ICP-OES	L-14	662		
	Waste A3	ICP-OES	L-3	15.0	16.6 \pm 2.2	13
ICP-OES		L-12	18.1			
Pb	Tap water	GFAAS	L-3	0.5	0.53 \pm 0.06	11
		GFAAS	L-12	0.6		
		GFAAS	L-13	0.5		
	Spring water	GFAAS	L-3	0.1	0.9 \pm 1.4	150
		GFAAS	L-12	2.6		
		GFAAS	L-13	0.1		
	River water	GFAAS	L-3	0.3	1.0 \pm 0.6	60
		GFAAS	L-12	1.3		
		GFAAS	L-13	1.3		
	Waste A1	ICP-OES	L-3	454	473 \pm 96	20
		ICP-OES	L-12	384		
		ICP-OES	L-13	445		
		ICP-OES	L-14	609		

respectively. The corresponding R.S.D. were 27%, 69%, and 11%, respectively. This feature indicates that the average quality of data obtained by direct GFAAS is generally good at above 10^1 ppb level; at 10^0 - 10^1 ppb level the data may be approximate ones; and should be regarded as not reliable at 10^{-1} - 10^0 level. In other words, the quality of data decreases as the concentration level is decreased as illustrated in Fig. 3.

The concentrations of Pb reported for the three samples were 0.53 ± 0.06 ppb, 0.9 ± 1.4 ppb, and 1.0 ± 0.6 ppb for the tap, spring, and river water respectively. The R.S.D. were 11%, 150%, and 60% respectively. Two out of three data sets exceeded the $\pm 25\%$ R.S.D. thresholds. This can be seen from the broad distribution of data as shown in Fig. 2. It must be pointed out that the average concentrations of Pb in these samples differed not so much, ranged between 0.5 and 1 ppb. However, their R.S.D. values differed widely between 10% and 150%. Whether such irreconcilability among various laboratories was due to contamination, chemical analysis difficulties, or others is, however, uncertain. Since data sets of spring water and river water showed

very large R.S.D. values larger than 60%, then whether the value of 11% for the tap water data set could be taken as a "good result" or not requires careful judgment.

Two waste water samples were analyzed by direct ICP-OES. The average concentrations reported were: Sample A1: 636 ± 48 ppb Cu, and 473 ± 96 ppb Pb; Sample A3: 16.6 ± 2.2 ppb Cu, and no Pb was detectable. The fact that the R.S.D. values of these sets of data were less than 25% was considered to be due to the relatively higher concentration level of the target elements in the samples.

Analysis of seawater

The seawater used for the inter-laboratory comparison was collected at 1000 m deep in the Luzon Channel, south of Taiwan. By referring the literature at the similar depth the concentration ranges for Cu and Pb were expected to be 0.1-0.2 ppb^{4,5} and 0.002-0.010 ppb⁶ respectively. Six laboratories participated in this cross-check, they were divided into two groups: Four laboratories applied pre-concentration procedures (CIX or SVX) before the detection, and the other two used direct methods. The results are listed in Table 6.

Table 6. Analysis of Cu and Pb in a 1000 m-deep Ocean Water

Element	Group	Methods	Lab code	Conc. (ppb) Mean \pm S.D.	Average value (ppb)	
					Mean \pm S.D.	RSD (%)
Cu	Pre-conc.	CIX-ICP-MS	L-1	0.17 \pm 0.05	0.17 \pm 0.10	55
		CIX-GFAAS	L-3	0.110 \pm 0.01		
		SVX-GFAAS	L-2	0.31 \pm 0.03		
		SVX-GFAAS	L-7	0.104 \pm 0.007		
	Direct	GFAAS	L-4	0.39 \pm 0.04		
Pb	Pre-conc.	FIA-ASV	L-9	0.27 \pm 0.15	0.38 \pm 0.41	108
		CIX-ICP-MS	L-1	0.20 \pm 0.04		
		SVX-GFAAS	L-2	0.30 \pm 0.04		
		CIX-GFAAS	L-3	0.046 \pm 0.007		
	Direct	SVX-GFAAS	L-7	0.98 \pm 0.12		
GFAAS	L-4	0.44 \pm 0.03				
	FIA-ASV	L-9	0.36 \pm 0.09			

The recently reported concentration ranges for Cu and Pb in the Pacific Ocean at 1000-m depth are 0.1-0.2 ppb and 0.002-0.004 ppb respectively.

For copper analysis the group using pre-concentration procedure provided a data range of 0.11-0.31 ppb (mean = 0.17 ± 0.01 ppb), three out of four data sets were within the expected range of 0.1-0.2 ppb. The out-lier (0.31 ± 0.03 ppb) was probably due to contamination during the analysis. The data reported by the direct group appeared in a little higher range (0.27 ± 0.15 and 0.39 ± 0.04 ppb; mean = 0.33 ± 0.08 ppb). The high estimation may be attributed to interference of high saline matrix to GFAAS; and the resolution of the FIA-ASV technique may not be satisfactory at this concentration level judging from the accompanied high R.S.D.

For lead analysis the reported data by the group using pre-concentration give a broad range (from 0.046-0.98 ppb), with a poor average R.S.D. of ca. $\pm 110\%$. The results from the direct measurements gave a similar data range (0.36 and 0.44 ppb). None of the data could match the nominated concentration range of 0.002-0.010 ppb. Even though, the precision for each laboratory was good (all individual R.S.D. were less than $\pm 25\%$), indicating that there existed serious systematic error in different laboratories. The reason was however not identified.

CONCLUSION

The present study gives a general aspect on the ability of determining Cu and Pb in environmental samples by randomly-selected analytical laboratories. Since there was no strict limitations on the choice of method, all participants could use the technique at their own comfort, therefore the

results may reflect the average quality of the environmental analysis in Taiwan.

For freshwater analysis at higher concentration levels (10 ppb or above for Cu and Pb), all laboratories were able to provide a reasonable precision and accuracy (within 25% thresholds). Direct measurements by instruments are preferred by many analysts because of the least maneuvering and least risk of contamination during the analytical processes. However, such direct measurements could only be applicable for samples containing less matrix compositions and comparatively higher concentrations (>10 ppb). At less-than-10 ppb level, the data reported from different laboratories may show scattered pattern. The variation exceeded frequently the thresholds of 25%, and the data at this level may be regarded as "approximate", or "semi-quantitative" unless the analyst can ensure the data quality by providing an accompanied QA/QC table during the analysis.

For seawater measurement at less than 1 ppb level, extreme care should be taken to avoid contamination. The laboratory should have enough experience in handling the seawater samples, otherwise the data reported should not be considered reliable.

ACKNOWLEDGMENT

This work was performed under the auspices of the National Science Council Contract No. NSC 81-0421-M-007-03. Grateful thanks are to the Environmental Protection Administration, Taipei Taiwan, for the permission of citing the data from the report⁷ numbered EPA 154820942.

Received May 25, 1995.

Key Words

Copper; Lead; Seawater; Inter-laboratory cross-check analysis.

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