The Determination of Some Toxic Elements in Drinking Water by Inductively Coupled Plasma Mass Spectrometry

[1]M.M. Rahman, [1]R.H. Ansary, [1]A.K. Azad and [2]A.M. Yusof

[1]Dept. of Pharm. Chemistry, Faculty of Pharmacy, International Islamic University Malaysia
25200 Indera Mohakota, Kuantan, Pahang, Malaysia
[2]Dept. of Chemistry, Faculty of Science, University Teknologi Malaysia, 81310 Skudai, JB, Malaysia

Abstract: A method is described for the determination of Cu, Cr, Cd, Pb, Sb, Se and As in drinking water using inductively coupled plasma mass spectrometry (ICP-MS). Samples were taken from water treatment plants of Negeri Sembilan and Melaka. Modified methods were developed for the trace determination of total inorganic arsenic, antimony, chromium, cadmium, selenium, lead, copper and mercury by ICP-MS. Detection limits obtained by ICP-MS for Cr, Cu, As, Se, Cd, Sb and Pb are 250, 66, 59, 48, 8, 85 and 3.28×10^3 ρg L^{-1} respectively. Calibration was accomplished by means of an aqueous calibration curve. The methods were verified by the analysis of quality control standard sample solutions.

Key words: Inductively coupled plasma mass spectroscopy (ICP-MS), drinking water, trace elements.

INTRODUCTION

The determination of trace elements in drinking water presents a challenge because of the low trace metal content and high matrix components. Although the detection power of inductively coupled plasma mass spectrometry (ICP-MS) permits direct determination of trace metals at sub-μg mL^{-1} levels, interferences from polyatomic species arising from the majors ions in drinking water prevent a simple analysis. There are also the problems that the concentrations of some of the elements are very low. A verity of methods to overcome these difficulties by means of preconcentration and matrix separation have been reported Heithmer, *et al* (1988), Jarvis, *et al* (1996) and Packer, *et al* (1997). In this work, a rapid method was developed for the multi-element trace metals in drinking water using ICP-MS detection by utilizing commercially available equipment and reagents.

METERIALS AND METHODS

Experimental:

The second method describes the multi-element determination of trace elements by ICP-MS Houk, *et al* (1980), Houk, R.S (1986) and Gray, *et al* (1983). Sample material in the solution was introduced by pneumatic nebulization into radiofrequency plasma where energy transfer processes cause disolvation, atomization and ionization. The ions were extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass to charge ratio by a quadruple mass spectrometer having a minimum resolution capability of 1 amu (atomic mass unit) peak width at 5% peak height. A continuous dynode electron multiplier detector and the ion information processor were processed by a data handling system registered the ions transmitted through the quadruple. Interferences relating to the technique must be recognized and were corrected. Such corrections might include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix was corrected by the use of internal standardization. In this work, we try to follow the recommended operating conditions provided by the manufacturer. When an electron multiplier detector was being used, precautions would be taken, where necessary, to prevent exposure to high ion flux. Otherwise changes in instrument responded to the multiplier might result.

Reagents and Consumable Materials:

Owing to the high sensitivity of ICP-MS, high-purity reagents have been used. In this method all acids used ultra high-purity grade. Nitric acid was preferred for ICP-MS in order to minimize polyatomic ion interferences. Concentrate nitric acid (Specific gravity 1.41-Merck) has been used to prepare nitric acid (1+1) and nitric acid (1+9). The former and the later acid solutions were consisted of 500 mL and 100 mL of concentrated nitric acid respectively with 400 mL of ASTM type 1 water and diluted to 1 L. ASTM type 1 water has been used for the preparation of all solutions and dilutions.

Corresponding Author: R.H. Ansary, Dept. of Pharm. Chemistry, Faculty of Pharmacy, International Islamic University Malaysia,25200 Indera Mohakota, Kuantan, Pahang, Malaysia.
E-mail: ansarychem@gmail.com

Preparation of Calibration Standards:

Fresh calibration standards were prepared every two weeks or as needed. Each of the standard stock solutions was diluted to levels appropriate to the operating range of the instrument using the appropriate acid diluents. The multi-element standard stock solution-3 was diluted to levels appropriate to the operating range of the instrument (ICP-MS) using ASTM type I water containing 1% (v/v) nitric acid. The instrument calibration was initially verified using a quality control sample. Known concentrations of standard solutions were used as a quality control sample to checkup the peak height or absorbance. If the peak height or absorbance of standard solutions were less than ± 10% of the calibration values, the samples were continued for analysis, otherwise they were discarded and the instrument was again calibrated with standard solutions. Two types of blanks were prepared for these methods. A calibration blank was used to establish the analytical calibration curve and the laboratory reagent blank (LRB) was used to assess possible contamination from the sample preparation procedure and to assess spectral background. All diluent acids were made from concentrated acids (concentration nitric acid and hydrochloric acid) and ASTM type I water. Solutions would be aspirated for 30 sec prior to the acquisition of data to allow equilibrium to be established.

Standardization and Calibration:

The proper operating configuration of instrument and data system were initiated and allowed a period of not less than 30 min for the instrument to warm up. The instrument was calibrated for the analyte to be determined using the calibration blank and calibration standards were prepared at four concentration levels within the linear dynamic range of analyte. Detection limits is defined as the concentration giving a signal equivalent to 3 times of the noise. Noise was calculated from the standard deviation of seven repetitive measurements of background intensity using a 3s integration time. Instrument detection limits (3σ) estimated from seven replicate integrations of blank (1% v/v nitric acid) following calibration of the instrument with three replicate integrations of a multi-element standard. Measured detection limits of ICP-MS were placed in the Table 1.

Table 1: Quality control standard sample solution results of ICP-MS.

Analyte	QCSS (μgL^{-1})	QC calculated Value (μgL^{-1})	Std. Dev %	% Recovery	IDL
Cu	2	1.99	0.54	99.9	0.066
	4	3.84	1.57	96.0	
	8	7.66	3.5	95.8	
	10	8.65	5.89	86.5	
As	2	1.99	0.52	99.9	0.059
	4	4.34	1.84	108.5	
	8	7.82	3.90	97.8	
	10	9.16	6.31	91.6	
Se	2	1.99	0.49	99.8	0.048
	4	4.31	1.82	107.8	
	8	7.95	3.92	99.4	
	10	9.21	6.63	92.1	
Cd	2	1.99	0.45	99.9	0.008
	4	4.24	1.69	106.0	
	8	7.73	3.67	96.6	
	10	9.00	5.98	90.0	
Sb	2	1.98	0.56	99.0	0.085
	4	4.80	2.20	120	
	8	8.92	4.39	111.50	
	10	10.30	3.86	103.0	
Pb	5	4.89	0.11	97.8	3.28
	10	11.83	0.13	118.3	
	25	26.28	0.33	105.9	
	50	52.94	0.38	105.1	
Cr	2	1.95	0.67	97.5	0.25
	4	4.39	1.70	109.8	
	8	8.10	3.65	101.3	
	10	9.626	6.61	96.3	

QCSS: -Quality control standard sample
IDL:- Instrument detection limit

Calibration and Standardization for ICP-MS Methods:

The adjusted spectrometer was shown a good performance resolution to produce a peak width of approximately 0.75 amu at 5% peak height (Thompson, *et al* (1987). Mass calibration was repeated if after adjustment it has shifted by more than 0.1 amu from unit mass. Instrument stability was demonstrated by running the tuning solution a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 5%. Priority was taken to initial calibration, set up proper instrument

software routines for quantitative analysis. The instrument was calibrated for the analytes to be determined using the calibration blank and calibration standards -3 and standard-1 prepared at four concentrations levels. Minimums of three replicate integrations were required for data acquisition. Linear calibration ranges were primarily detectors limited. The upper limit of the linear calibration range were established for each analyte by determining the signal responses from a minimum of four different standards concentration, one of which was close to the upper limit of the linear range. Care would be taken to avoid potential damage to the detector during this process.

Procedure of Samples Analyses:

For the determination of trace elements in drinking water and raw (surface) waters, 100 mL aliquot of the filtered acid preserved sample was taken, and 1 mL of concentrated nitric acid was added. Allowance for sample dilution would be made in the calculations. The instrument software run procedures were established for quantitative analysis. For all sample analyses, a minimum three replicate integration was required for data acquisition. Any integration was discarded, which were considered to be statistical outliers and the average of the integration for data reporting was used. Sufficient time was allowed to remove traces of the previous sample. Samples would be aspirated for 30 sec prior to the collection of data. Samples having concentrations higher than the established linear dynamic range should be diluted into range and reanalyzed. The sample was analyzed for the trace elements, protecting the detector from the high concentration elements.

Precision and Accuracy of ICP-MS Methods:

The sample mean spike percent recovery, the standard deviation, the average percent recovery and the relative percent different between the duplicate determinations were listed in Table-1. Estimated and calculated detection limits of instrument were listed in Table 2.

Table 2: Estimated instrument detection limits and calculated detection limits.

Analyte	Recommended mass	Estimated IDL($\rho g L^{-1}$)	Calculated IDL($\rho g L^{-1}$)
Cr	52	10	250
Cu	63	10	66
As	75	10	59
Se	82	100	48
Cd	111	10	8
Sb	123	<1	85
Pb	208	<1	3.3×10^{-3}

IDL- Instrument Detection Limits and Calculated Detection Limits.

RESULTS AND DISCUSSION

The element concentrations below the determined IDL have not been reported in this work. Aqueous sample concentrations were multiplied by the appropriate dilution factor. The data was rounded to the sixth decimal place and reported as $\mu g L^{-1}$ up to two significant figures. The QC data obtained during the analyses indicates the quality of the sample data which have been submitted with the sample results. The main objective of this work was to assess the current state of accumulation of major pollutants due to heavy and trace elements in water from water treatment plants of Negeri Sembilan and Melaka. This study will one hopes; helps the responsible authorities to establish baseline data for future reference. The determination of heavy and trace metals concentrations is imperative in checking their toxicity in relation to different source of water such as ground water, surface water, seawater and drinking water. Airborne pollutants such as As, Se, Sb, and Pb take some time to dissolve in the water and finally these will enter into the human beings through consumption. Samples were taken from treatment plants, a total of four treated, four pretreated and four raw water samples were collected for the analysis. The idea is to evaluate the efficiency of the treatment process in reducing the heavy and trace metals (toxic) contents. The nature of activities in the vicinity of the reservoirs or rivers feeding the treatment plants have a profound effect on the heavy and trace metals concentrations in the samples. Concentrations of dissolved trace elements such as As, Se, Sb, Cd, Cr, Cu and Pb determined in drinking water are reported in Table 3 and their position were showed in Figures (1, 2, 3 and 4). The majority of the samples were not diluted except chromium. The presence of As relatively higher amounts found in all raw water samples. After pretreatment and treatment, As contents were reduced in all plants. Table 3 shows the presence of Cr are relatively higher amounts except raw water of new plant (i.e., river of Sungai Terip at Negeri Sembilan). Raw water at this plant contains very low amounts of Cr but after treatment, the contents of Cr are higher than that of raw water. In this case, the water was contaminated by either dosing chemicals or treatment tanks and pipelines or both. This amount is negligible according to drinking water guideline (50 $\mu g\ L^{-1}$) given by WHO (Drinking Water Guideline (1992). The raw water fed into this new plant was taken from Sungai Terip at Negeri Sembilan, was found to be polluted by Cr. This pollutant may be discharged from the industrial area up stream. Treatment plants in Melaka (new and old) both functioned well in reducing the Cr contents. For

reducing Cr and Pb, the new treatment plants in Negeri Sembilan, was not found to be more efficient. The presence of Cu relatively higher amounts was found in all raw water samples compared to pretreated and treated waters. After pretreatment and treatment, the Cu contents were reduced significantly in all plants except the new plant in Melaka. In this plant, fresh water (FW-3) was slightly contaminated possibility due to dosing chemicals and in the pipelines. The Presence of Pb in higher amounts except raw water of the new plant (i.e., river of Sungai Terip at Negeri Sembilan). Raw water at this plant contains very low amounts of Pb but after treatment, the contents of Pb in fresh water (FW-2) are higher than that of raw water. In this case, the water was contaminated by either dosing chemicals or treatment tanks and pipelines or both. This amount is also negligible according to drinking water guideline 10 μg L^{-1} given by WHO [8]. From the Table 3, it is clear that the amount of others trace elements (i.e., Se, Sb and Cd) are too low in all water samples. In this study, speciation of As and Cr is possible, but the speciation of Sb and Se is a very difficult task. Because of, in this study, the samples contain very low level of these elements. The presences of Cu, Cd and Pb in all water samples are less than the amount recommended by Interim national water quality control (INWQC) and WHO, guideline (Drinking Water Guideline (1992), Yusof, A.M (1997). So, it is clear that the supplied water samples of above mentioned plants are safe for public use.

Table 3: Results obtained by using ICP-MS methods.

Analyte	Cu (μgL^{-1})	As (μgL^{-1})L	Se (μgL^{-1})	Cd (μgL^{-1})	Sb (μgL^{-1})	Pb (μgL^{-1})	Cr (μgL^{-1})
RW-1	2.61±1.6	10.97±7.2	0.49±0.3	0.13±0.1	1.41±0.85	1.49±0.8	16.92±11.4
PW-1	2.10±1.5	3.13±2.4	0.22±0.2	0.08±0.1	0.64±0.42	0.48±0.3	0.52*±0.3
FW-1	1.94±1.1	2.69±1.6	0.13±0.1	0.11±0.1	0.41±0.35	0.46±0.2	11.79±7.3
RW-2	1.39±1.0	8.69±7.2	0.15±0.12	0.04±0.01	0.33±0.14	0.63±0.5	0.57*±0.3
PW-2	0.74±0.17	1.14±0.3	0.12±0.03	0.07±0.01	0.25±00.05	0.42±0.09	5.86±1.18
FW-2	1.54±0.62	0.98±0.43	0.12±0.06	0.09±0.03	0.32±0.16	0.80±0.29	4.35±1.8
RW-3	3.64±1.16	0.74±0.25	0.17±0.06	0.07±0.02	0.26±0.08	3.17±0.99	28.62±8.93
PW-3	1.47±0.41	0.64±0.19	0.11±0.03	0.05±0.01	0.23±0.09	0.40±0.08	1.69±0.43
FW-3	2.81±0.24	0.52±0.11	0.13±0.03	0.04±0.01	0.63±0.23	0.57±0.12	0.91*±0.24
RW-4	5.07±2.52	5.95±2.82	0.17±0.13	0.26±0.13	0.22±0.12	3.52±1.13	50.09±18.9
PW-4	1.41±0.92	4.52±2.71	ND	0.07±0.05	0.31±0.19	2.39±1.33	11.13±6.99
FW-4	1.12±0.66	2.92±2.03	0.1±0.05	0.02±0.01	0.20±0.12	1.07±0.43	3.39±1.90

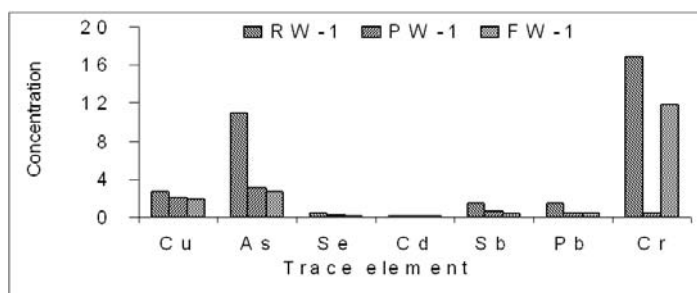RW= Raw Water, PW= Pretreated Water, FW= Fresh Water

Fig. 1: Trace element distributions of old water treatment plant in Negeri Sembilan by ICP-MS.
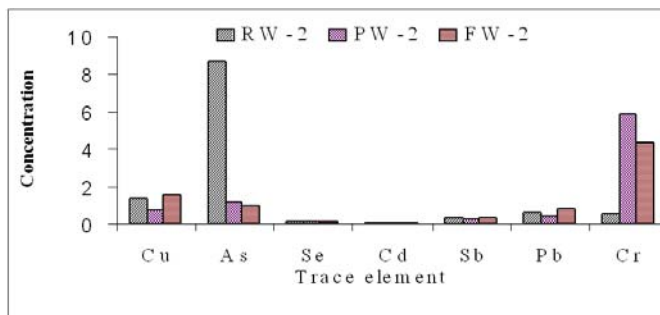

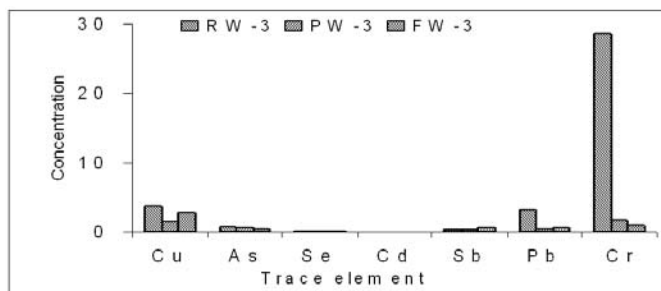**Fig. 2:** Trace element distribution of new water treatment plant in Negeri Sembilan by ICP-MS.

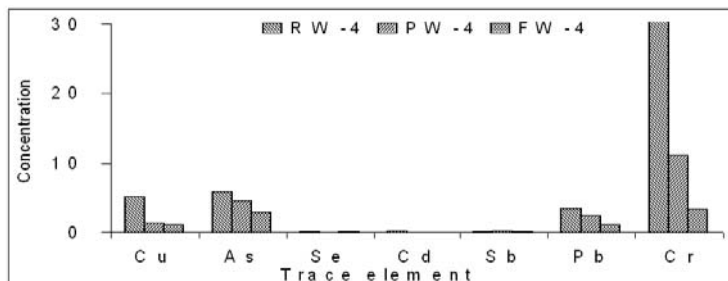**Fig. 3:** Trace element distributions of old water treatment plant in Melaka by ICP-MS.

Fig. 4: Trace element distribution of new water treatment plant in Melaka by ICP-MS.

Scope and Application of ICP-MS:

This method is rapidly gaining acceptance in the environmental application area. The analytical capability of the instrument matches the needs of newer environmental requirements. This method provides procedures for determination of dissolved elements in ground waters, surface waters and drinking water. It may also be used for the determination of total recoverable element concentrations in these water as well as waste water, sludge and solid waste samples. Dissolved elements are determined after suitable filtration and acid preservation. In order to reduce potential interferences, dissolved solids would not exceed 0.2% (w/v). This method is applicable to the determination of the following elements aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, thallium, thorium, uranium, vanadium, tin and zinc according to their detection limits. Estimated instrument detection limits (IDLs) for these elements are listed in Table 2. These are intended as a guide to instrumental limits typical of a system optimized for multielement determinations and employing commercial instrumentation and pneumatic nebulization sample introduction.

Conclusion:

ICP-MS provides a simple, rapid and accurate technique for the routine determination of heavy and trace elements such as As, Sb, Se, Pb, Cr, Cd, and Cu analysis of natural (drinking) water samples. The technique seems to provide a solution to the rapid routine quantitative analysis (approximately 390 determinations/ day) in high productivity laboratory environment (Pruszkowski, et. al (1998)]. Data presented in this paper show that the accuracy of the method compares favorably with established and recognized techniques, ICP-MS, in terms of both sensitivity and precision. In addition, no special sample pretreatment or preparation is required other than routine field filtration preservation techniques. The effectiveness of the ICP-MS system in the alleviation of heavy and trace metal interferences was demonstrated and the ability to perform highly quantitative analysis of trace elements at low ambient-concentration levels at a very high sample production rate is unique. ICP-MS has the additional advantage of being able to determine high and low level concentrations in the same analysis. However, at the low concentrations of the analytes in these samples, clean laboratory procedures are imperative to attain goods result.

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