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Determination of Lead, Cadmium and Silver in Industrial Wastewater of Riyadh, Saudi Arabia by SIA/ICP/MS Technique

Naser Mohammed Al-Andis
Department of Chemistry, College of Science, King Saud University
PO Box 2455 Riyadh-11451,Kingdom of Saudi Arabia
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Abstract. Standard addition method and SIA/ICP/MS technique were used for the determination of Pb, Cd and Ag in wastewater samples collected from Riyadh industrial area II. Recovery of the added elements was 95-97% and percentage relative standard deviation values were less than 3% in all cases. The concentration of 14.6 and 34.4 μg Pb/L, 2.5 and 5.4 μg Cd/L and 2.1 and 3.8 μg Ag/L in raw and reused wastewater samples were determined, respectively. The results were compared to international allowable concentrations of trace elements in water and found to be within acceptable levels.

Key Words : Wastewater, SIA/ICP/MS, Pb, Cd, Ag.

Introduction

Environmental pollution is a universal problem these days and the studies concerning toxic heavy metals in wastewater have a great role in this field. Manufacturing activities in industrial areas can introduce dangerous pollutants into wastewater system e.g. toxic elements [1].They are soluble in water as ions and readily absorbed into the body .Pb ,Cd and Ag are particularly interesting because they are widely used in industry particularly in metal working or metal working plating shops and in such products as batteries and electronics [2]. It has been reported , Pb causes metal retardation, Ag may produce argyria and Cd caused nausea and vomiting. Therefore, detection of these elements dissolved in wastewater is necessary for environmental studies and public health. The principles, developments and applications of flow injection analysis (FIA) were widely used[3]. A sequential injection has been introduced as a new technique for sample introduction in the field of analytical chemistry [4]. This technique is coupled

recently with inductively coupled plasma mass spectrometry (ICP/MS) for trace elements analysis[5]. This technique is fully automated, sensitive, rapid, uses small sample volumes, with multi-element analysis capability, is relatively free from interferences and gives low detection limits for most elements when compared to other techniques[6-9]. All these advantages makes it suitable to use SIA/ICP/MS in this study for the determination of Pb, Cd and Ag in raw and reused(treated) waste water samples collected from Riyadh industrial area II, Saudi Arabia.

Experimental

Apparatus: Modular Injection System MIS-1 (Alitea, USA) was used as sample introduction technique for sequential injection analysis (SIA). Teflon tubings used for MIS, were 30 cm of 0.8 mm i.d. for carrier solution, 160 cm of 0.8 mm i.d. for holding coil, 5 cm of 0.5 mm i.d. connected to port 2 for sample, 10 cm of 0.8 mm i.d. is connected from port 1 to the concentric nebulizer into ICP/MS and 15 cm Tygoon tubing was used for the pump (all tubings are supplied by Upchurch Scientific Inc.[4]. The MIS is operated by Alitea's FIA Lab software and an IBM compatible personal computer and the operating instructions are followed as in MIS manual for SIA [10]. Table 1 includes FIA lab software method entries used for Alitea MIS-I SIA system.

Table 1. FIA Lab software entries for Alitea MIS-1 Sequential Injection System

i.d.	Time(s)	Duration(s)	Pump 1	Valve 1	Data
1	0.0	5	100	home	on
2	5.0	3	-100	2	on
3	8.0	4	100	10	on
4	12.0	3	-100	2	on
5	15.0	5	100	home	on

An inductively coupled plasma mass spectrometer model 250 (Sciex Elan) with a multiple elements program is used with a 15 BC 012B computer with by Matrox Electronic System Ltd. and a plotter by Houston A schematic diagram of the MIS-1 coupled with ICP/MS is shown in Figure 1 and the operating onditions for ICP/MS are listed in Table 2.

Table 2. Instrumental operating conditions for Elan ICP/MS

R.F. incident power	1.2 kw	Sample flow	60 μL/sec
Plasma gas flow	13 L/min	Resolution	Low
Auxiliary gas flow	1.4 L/min	Threshold	1
Nebulizer gas pressure	40 psi	Counting precision	0.1
Measurements per peak	5	Measurements time ,sec.	0.05
Repeats per integration	5		

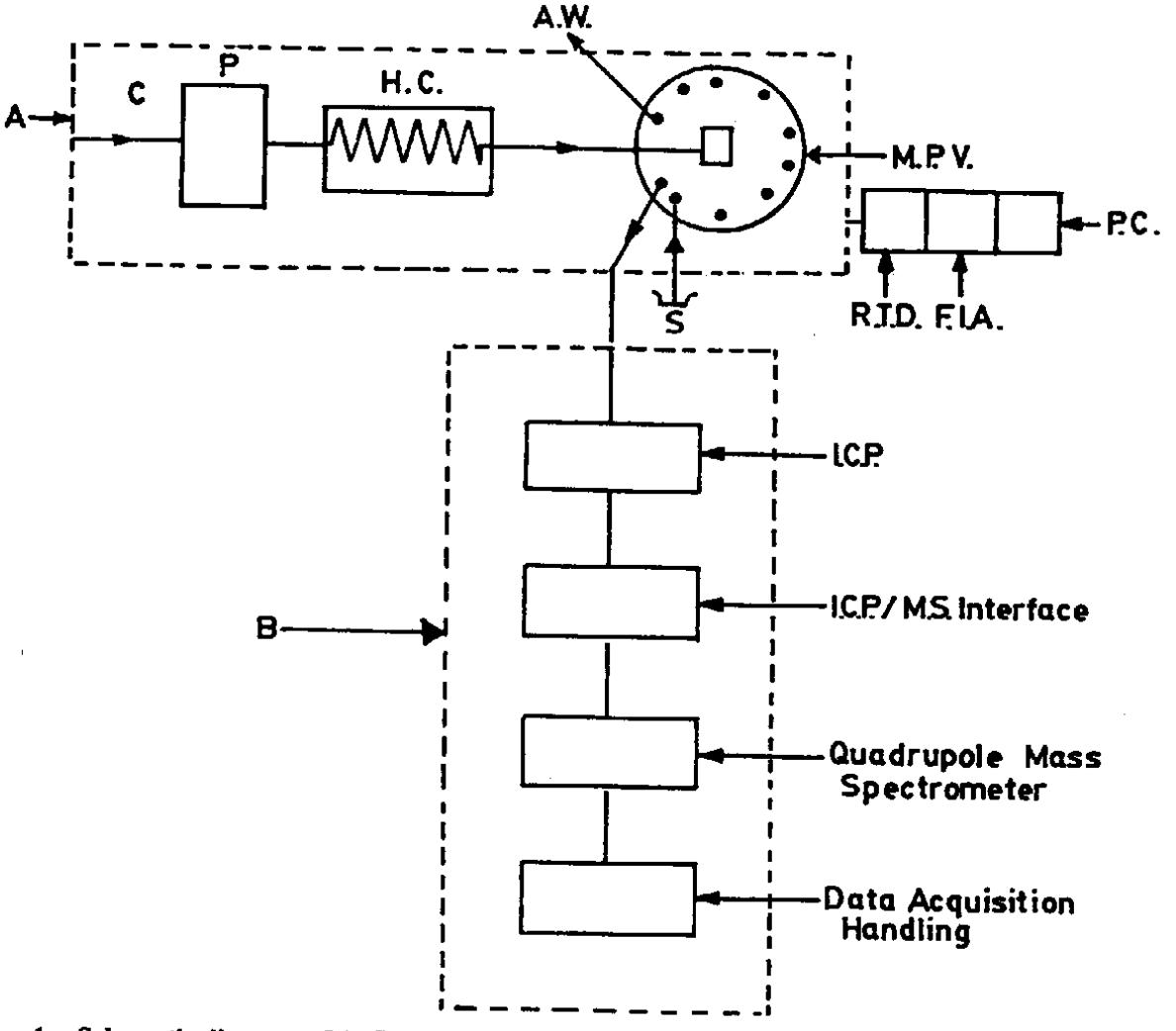

Fig. 1. Schematic diagram of A; Sequential injection system (S.I.) coupled with B: Inductively coupled plasma mas spectrometer (I.C.P./M.S.). (C. for sample, M.P.V. for multi position value, R.T.D. for R.T.D. A.D.A.-100 interface card, F.I.A. for alitea, F.I.A. lab software and P.C. for I.B.M. copatible personal computer), [2].

Reagents and samples: Nitric acid solutions of 50%(v/v) and 3% (v/v) were prepared from concentrated analar nitric acid, sp.gr. 1.42, 69-71% (BDH Chemicals Ltd.,Poole, U.K.). High purity chemicals of lead nitrate, cadmium oxide and silver nitrate supplied from Spex Industries Inc., USA were used for preparing stock solutions. Multielement standard solution of 2.5 μg Pb/ml, 0.5 μg Cd/ml and 0.5 μg Ag/ml was prepared from stock solution by appropriate dilution. Deionized distilled water was obtained using a Corning Mega-pure water distillation apparatus, model MP3.

During five month period, wastewater samples before and after treatment (Five replicates of each) were collected from sewage system station of Riyadh industrial area II(40 Km south from city center). Some general properties of these samples are included in Table 3.

Table 3. Some general properties or wastewater sample

	Raw sample	Reused (treated) sample
Flow, average cubic meter/day	14000	13-213
pH	5-11	6-8
Biochemical oxygen demand (BOD) (mg/L)	350	30
Suspended Solids, 58 (mg/L)	350	14.5

Procedure: Well shaken and filtered (whatman paper No.41) wastewater samples (before and after treatment) of exactly 20 ml were transfered to four separate volumetric flasks (25 ml). To each flask, 1-5 ml of 50% (v/v) nitric acid solution was added. Flasks No.1, 2, 3 and 4 were spiked with 0, 0.5, 1 and 1.5 ml of the multielement standard solution which contains 2.5 μg Pb/ml, 0.5 μg Cd/ml and 0.5 μg Ag/ml. The contents were then diluted to the mark with deionized distilled water to give final concentrations of 0, 50, 100 and 150 μg/L for Pb and 0, 10, 20, and 30 μg/L for Cd and Ag.

All the solutions of Pb, Cd and Ag were aspirated at 60 μL/sec. using 3%(v/v) nitric acid as a carrier solution through SIA/ICP/MS technique. Multiple elements program associated with Elan ICP/MS by SCIEX was used for plotting the peaks of the analyzed elements.

Results and Discussion

Detection of toxic elements such as Pb, Cd and Ag in industrial wastewater samples using sensitive analytical procedure is necessary. The use of standard addition method and SIA/ICP/MS technique will solve sample matrix problems and give accurate results especially at μg/L levels of trace elements[11,12].

Traces of time (min.) against intensity (ions/sec) for solutions of the sample only and the sample with added elements were obtained. Typical peaks for Pb in raw and reused waste water samples are shown in Figure 2. Standard addition graphs extracted from these plotted peaks for Pb, Cd and Ag in wastewater samples appear in Figure 3. These graphs are very linear with correlation coefficient values range of 0.995-0.997 (Table 4). The standard deviation based on a resulting for five replicate samples measurements are calculated and found to be, 0.47 for Pb, 0.13 for Cd and 0.11 for Ag as included in Table 4. Percentage recovery values for the added elements were 97% for Pb and 95% for both Cd and Ag (Table 4).

Table 4. Statistical data for Pb, Cd, and Ag in wastewater (Reused) sample by SIA/ICP/MS

Element	Added(a)	Found(a)	%Recovery	S.D.(b)	Corr. coeff.
Pb	50	48.5	97	0.47	0.997
Cd	10	9.5	95	0.13	0.966
Ag	10	9.5	95	0.11	0.995

(a) Units are in μg/L

(b) SD = Standard deviation for five replicates

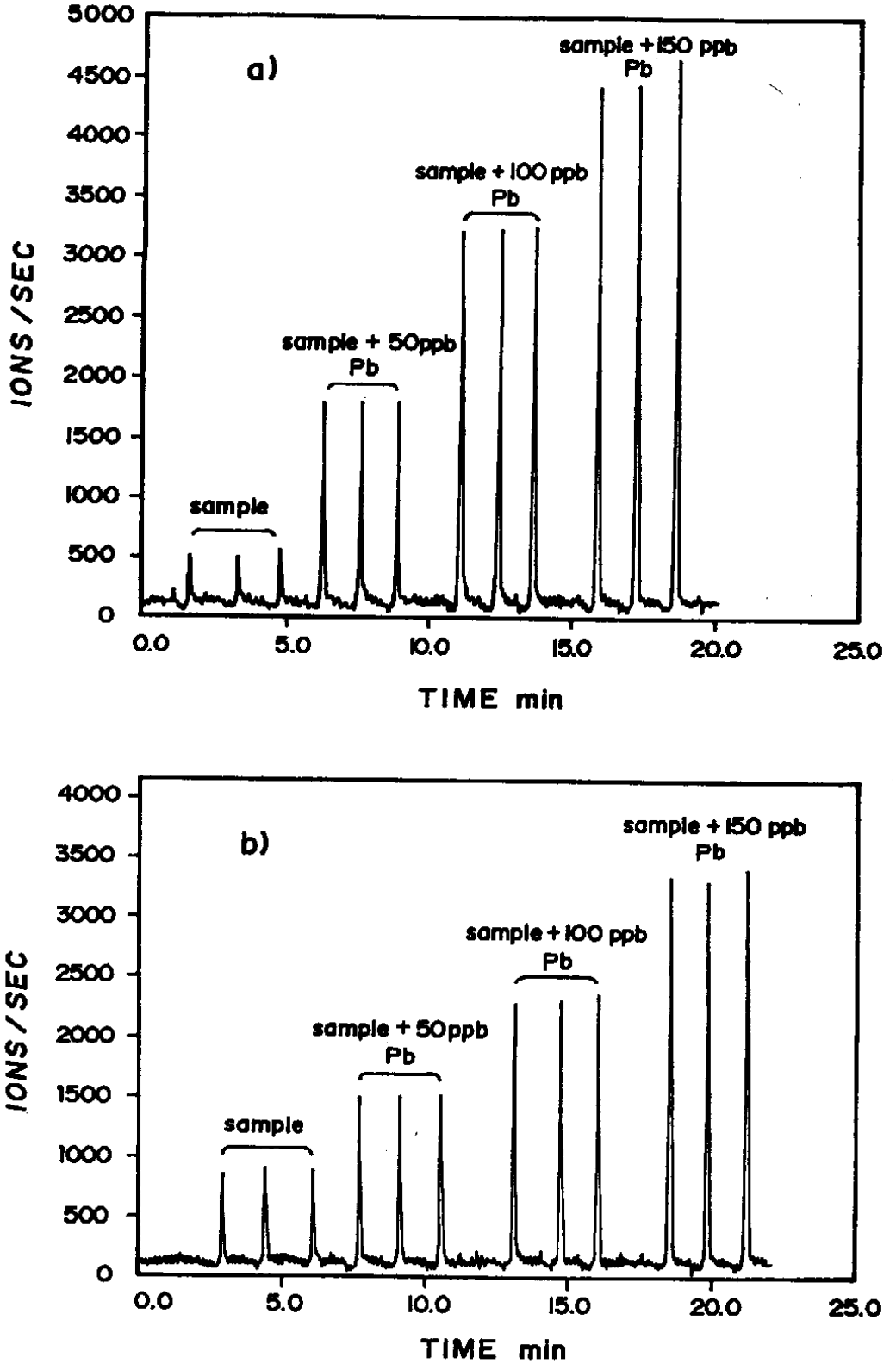

Fig. 2. Typical peaks obtained for lead in a) raw and b) reused waste water samples using SIA/ICP/MS technique.

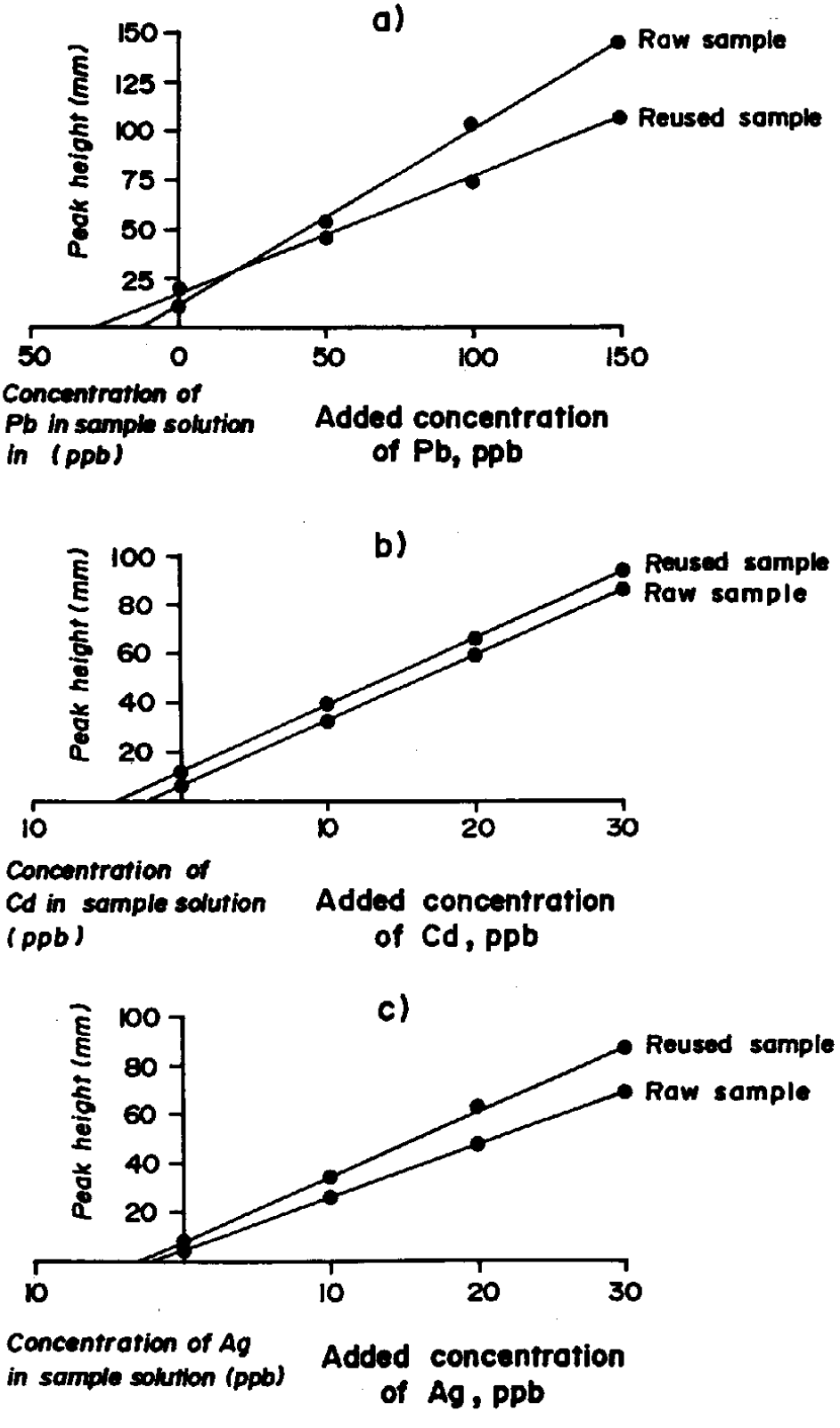

Fig. 3. Standard addition graphs obtained for a) lead, b) cadmium and c) silver in waste water samples using SIA/ICP/MS.

The mean concentrations and percentage relative standard deviations were 14.6 μg Pb/L ±1.2 ,2.5μg Cd/L ±2.7 and 2.1 μg Ag/L ±2.9 in raw waste water sample and were 34.4 μg Pb/L ±1.4, 5.4 μg Cd/L ±2.6 and 3.8 μg Ag/L ±2.9 in reused waste water sample(Table 5). The increase of concentrations from raw to reused samples observed may be related to the procedure of wastewater treatment used at the plant, the evaporation of sample will increase the concentration of the dissolved ions and the contamination caused by the addition of commercial reagents.

USEPA estimated that community water system must have concentrations of Pb less than 5 μg/L .The Cd concentrations of U.S. drinking water have been reported 8.2 μg/L (mean) and recommends Ag to be 50 μg/L in domestic supply.

The maximum concentration limits stated by Saudi Arabian Standards Organization (SASO) for bottled and unbottled drinking water are 50 μg/L for Pb, 10 μg/L for Cd and 50 μg/L for Ag (Table 5) [13].

Table 5. Concentration(a) (μg/L) ±RSD(b) of Pb, Cd and Ag in industrial wastewater by SIA/ICP/MS

Element	Sample		Maximum limits	
	Raw	Reused	USEPA[c]	SASO[d]
Pb	14.6 ± 1.2 %	34.4 ± 1.4%	50.0	50.0
Cd	2.5 ± 2.7 %	5.4 ± 2.6 %	8.2	10.0
Ag	2.1 ± 2.9 %	3.8 ± 2.9 %	50.0	50.0

(a) mean for five replicate sample measurements
(b) RSD for relative standard deviation
(c) US Environmental Protection Agency
(d) Saudi Arabian Standards Organization

Conclusion

The standard addition SIA/ICP/MS method proves to be sensitive, accurate and reliable for the measurement of these toxic elements at ?g/L levels. Although there was an increase in the concentration of these elements after treatment which was not due to the method of analysis but to evaporation and contamination of treated wastewater. The concentrations of trace Pb, Cd and Ag obtained in wastewater samples before and after treatment was found to be within international acceptable level.

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تقدير الرصاص ، الكادميوم والفضة في مخلفات مياه المنطقة الصناعية بالرياض ، المملكة العربية السعودية " التحليل الحقني المتتابع – الحث الطيفي المزدوج – طيف الكتلة "

ناصر محمد العنقس

قسم الكيمياء ، كلية العلوم ، جامعة الملك سعود ،

ص. ب. ٢٤٥٥ ، الرياض ١١٤٥١ ، المملكة العربية السعودية

(استلم في ١٤١٧/٥/٥ هـ ، و قبل للنشر في ١٤١٨/٢/١٦ هـ)

ملخص البحث. استخدمت طريقة الإضافة القياسية ، تقنية التحليل الحقني المتتابع ، الحث الطيفي المزدوج ، وطيف الكتلة لتحديد كمية الرصاص ، الكادميوم والفضة في عينات من مياه مجاري المنطقة الصناعية الثانية بالرياض (المملكة العربية السعودية) . أعطت النتائج نسبة استخلاص مئوية من ٩٥٪ إلى ٩٧٪ والنسبة المئوية للانحراف المعياري النسبي أقل من ٣٪ في كل القياسات وكانت التراكيز بوحدة الميكروجرام للتر في المياه غير المعالجة والمعالجة على التوالي هي ١٤ر٦ ٪ و ٣٤ر٤٪ للرصاص ، ٢ر٥٪ و ٤ر٥٪ للكادميوم ، و ٢ر١٪ و ٣ر٨٪ للفضة . عند المقارنة بين مستويات هذه المعادن في العينات مع الحدود المسموح بها عالميا وجد أنها عند المستوي المقبول .