

Validation of an extraction technique based on Tributyl Phosphate for the determination of Pb(II) in water

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Abstract

An extraction technique using tri-butyl phosphate was developed and validated for a speciation study of lead in aqueous environment. The extraction was found to be optimum at pH 9 – 11, shaking time of 2 – 5 minutes and 0.04M HNO₃ as stripping agent. The validation criteria include recovery, linearity, accuracy, precision, instrument detection limit (IDL), method detection limit (MDL), limit of quantifications (LOQ), measurements of uncertainty for test result, robustness and ruggedness. An Inductively Couple Plasma-Optical Emission Spectrometry (ICP-OES) was used to the Pb in this study. At the optimal conditions the technique shows high accuracy and good linearity with a correlation coefficient of 0.9969 for the calibration curve. This method is very sensitive and has good precision with IDL of 3.71 µg/l, MDL of 4.43 µg/l and LOQ of 14.75 µg/l and with mean relative standard deviation (RSD) of less than 20 %. Mean recovery of almost 100% was achieved. This method also shows moderate robustness and ruggedness. Application of the method to water samples from six stations of Langat River has shown that the percentages of Pb²⁺, included Pb(OH)⁺, Pb(OH)₂ and Pb(OH)₃⁻ in a dissolved fraction varied in the range of 64 - 80 %.

Abstrak

Satu kaedah pengekstrakan menggunakan tri-butyl fosfat telah dikembangkan dan divalidasi bagi kajian penspesiesan plumbum dalam persekitaran akuatik. Kaedah pengekstrakan ini adalah optimum pada pH 9 – 11, masa goncangan 2 – 5 minit dan dengan HNO₃ 0.04 M sebagai agen perlucutan. Kriteria validasi yang digunakan termasuklah perolehan semula, kelinearan, kejituan, kepersisan, had pengesanan instrumen (IDL), had pengesanan kaedah (MDL), had kuantitatif (LOQ), ukuran ketidakpastian, keteguhan dan kelasakan. Kaedah Spektrometer Pancaran Optik-Plasma Gandingan Aruhan (ICP-OES) telah digunakan untuk menentukan Pb dalam kajian ini. Pada keadaan optimum, kaedah pengekstrakan ini mempunyai kejituan yang tinggi dan kelinearan yang baik dengan pekali korelasi 0.9969 bagi lengkung tentukuran. Kaedah ini juga amat peka dan mempunyai kepersisan yang baik dengan IDL 3.71 µg/l, MDL 4.43 µg/l dan LOQ 14.75 µg/l dan dengan min sisihan piawai relatif kurang daripada 20 %. Min pemulihan semula menghampiri 100% dan kaedah ini juga didapati agak teguh dan lasak. Penggunaan kaedah ini bagi menganalisis plumbum di enam stesen sepanjang Sungai Langat menunjukkan kehadiran plumbum larut Pb²⁺ iaitu termasuk spesies Pb(OH)⁺, Pb(OH)₂ dan Pb(OH)₃⁻ dalam julat 64-80% daripada keseluruhan Pb dalam pecahan larut.

Keywords : Validation, speciation , extraction, heavy metal and lead.

Introduction

The extracting power of tri-butyl phosphate (TBP) for actinides was noted by workers in the wartime Manhattan Project in the U.S.A at least as early as 1944, when they found that it is able to extract thorium and plutonium [1]. The outstanding success of TBP in the nuclear industry has proved a great stimulus to the introduction of solvent extraction processes into extractive metallurgy. Pb is an important element from both industrial and environmental points of view. The hazardous effects of lead for man and environment are well known. Chronic exposure to lead causes nephritis, scarring and the shrinking of kidney issues. Thus, the separation and determination of lead from the desired constituents is of utmost importance.

Literature survey shows various solvent extraction methods for the separation and preconcentration of Pb(II). Different reagents such as 2-ethylhexylphosphoric acid monoester[2], triphenylphosphine oxide [3], mesityl oxide [4], aliquat 336, alamine 336 [5], trioctylamine [6], hexafluoroacetylacetone & dibutylsulphoxide [7], thio-2-theonyltrifluoroacetone [8], tributyl phosphate [9], amberlite LA-1 [10] and Cyanex 302 [11] have been reported for extraction of Pb(II). Study about solvent extraction of Pb(II) with TBP was doing by Yadav [9]. It is shown that Pb(II) can be 100% extracted by 30% TBP in isobutyl methyl ketone (IBMK) from 3.0 M hydrochloric acid/2.0M Lithium chloride. Lithium chloride was used as the salting out agent and water was used as stripping agent of Pb(II). In this research, a new method for the solvent extraction

separation of Pb(II) with TBP has been developed. It is found that TBP could extracted 100% Pb(II) from the aqueous solution in the optimum conditions. The optimum conditions are 9-11 for pH, 0.04 M for nitric acid, HNO_3 concentration and 2-5 minutes shaking time. HNO_3 0.04 M was used as stripping agent [12]. Compared to Yadav [9], this method has the advantages because it was doing in the aqueous situation and did not use salting out agent.

This new extraction method of Pb(II) by TBP should be validate. Method validation is a process for establishing that performance characteristics of the analytical method are suitable for the intended application [13]. Method validation is also a process of verifying a method if it is fit for a purpose [14]. This included process of establishing performance and limitations of the method i.e. the extent to which analytes can be determined in terms of precision and accuracy in the presence of interferences. The aim of this work is to validate the procedure of extraction based on tri-butyl phosphate for the determination of Pb(II) with Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES). The validation criteria include recovery, linearity, accuracy, precision, instrument detection limit (IDL), method detection limit (MDL), limit of quantifications (LOQ), measurements of uncertainty for test result, robustness and ruggedness.

Experimental

Instruments

An ICP-OES (Optima Perkin Elmer 4300 DV) was used for Pb analysis. A digital pH meter (Fisher Scientific Model AB 15) was used to determine the pH of test solutions. The buffer solutions at pH values of 4, 7 and 9 were used to standardized the pH meter used.

Reagents

A stock solution of Pb(II) was prepared by dissolving 1.59 g of $\text{Pb}(\text{NO}_3)_2$ and make up to 1000 ml with de-ionized water containing 2.0 ml of concentrated HNO_3 . The solution was standardized complexometrically using EDTA [15] and working solutions of lower concentrations were prepared by suitable dilutions. Tributyl phosphate (100% 3.66M) without dilution was used in the extraction. All reagents used were of analytical reagent grade.

General Procedure

An aliquot of solution containing Pb(II) was pipetted into 25 ml volumetric flask and its pH was adjusted to 10.0 with dilute nitric acid and ammonium hydroxide [11]. The total volume was made to 25 ml and transferred to a separatory funnel and shaken with 1 ml tri-butyl phosphate (TBP) for 3 minutes. After separating the two phases, Pb(II) was back extracted from the organic phase by shaking with 10 ml 0.04 M nitric acid and determined by ICP-OES. All of the extraction was carried out at the optimum conditions. The optimum conditions are 9-11 for pH, 0.04 M for nitric acid, HNO_3 concentration and 2-5 minutes for shaking time [12].

Results and Discussion

Linearity

The linearity of an analytical method is defined as the ability of the method to obtain test results proportional to the concentration of analyte in the sample [14]. To check the linearity of this method, a range of Pb(II) standards solution in de-ionized water at the concentrations of 10, 20, 40, 60, 80, 100 $\mu\text{g/l}$ were extracted at the optimum conditions. A linear fit was obtained using the linear least squares regression procedure. The coefficient of determination (R^2) for this method is 0.9969, indicating an excellent linearity relationship between Pb(II) and the detector response as shown in Figure 1. The intercept, 43.879 is occurred because 0.04 M HNO_3 is used as a blank in the ICP-OES determination.

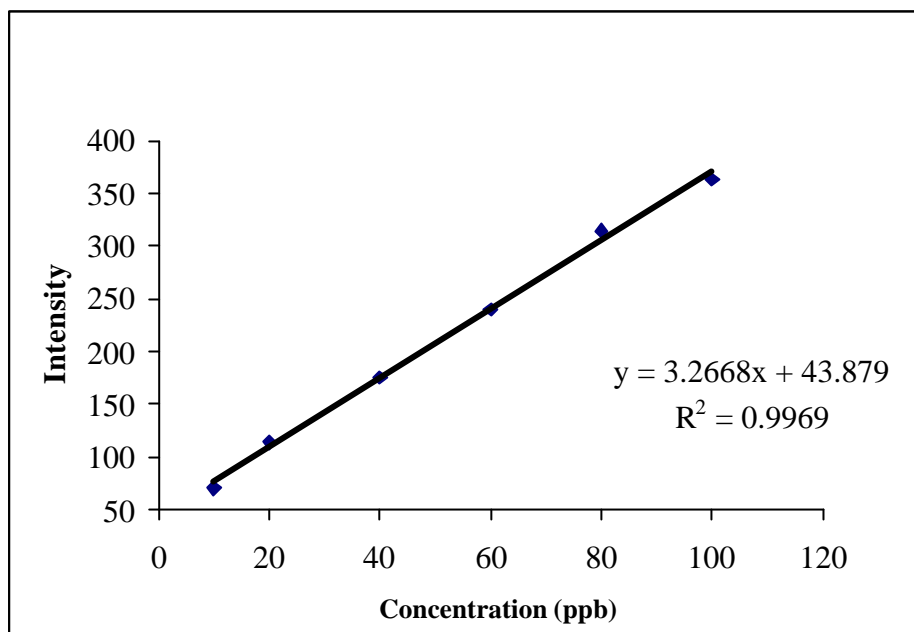


Figure 1 : Linearity graph for the extraction of Pb(II)

Pb(II) Recoveries

Water samples containing of 5, 10, 20, 40 and 100 µg/l Pb(II) respectively were prepared. The water samples were then extracted according to the general procedure at the optimum conditions. Seven replicate measurements were carried out for each test. As can be seen from the recovery results shown in Table 1, the Pb(II) was recovered in the range of 100 to 110 % for the concentration levels between 5 to 100 µg/l. The percentage of relative standard deviation (%RSD) ranging from 8.67 to 25.00 was obtained for the above stated concentration.

Table 1: Mean Recovery (%) Extraction of Pb(II) with Tributyl Phosphate from spiking water samples analyzed by ICP-OES.

Spiking level (µg/l)	Mean Recovery (%)	% RSD
5	110.00	25.00
10	104.90	20.98
20	103.58	14.74
40	101.20	12.56
100	100.00	8.67

Mean recovery obtained from 7 replicates of analyses

Accuracy and Precision

Accuracy is the closeness of the test results obtained by the method to the true value. It is often calculated as the percent recovery of the known amount of analyte in the sample [14]. The accuracy was determined by spiking known amounts of analyte to water samples across the specified range of the analytical procedure to obtain 10, 20, 40, 60, 80 and 100 µg/l concentrations. The linearity graph in Figure 1 shows a good accuracy with correlation coefficient of 0.9969.

As for the term of precision, the ISO defined it as the closeness of agreement between independent test results obtained under the stipulated conditions [13]. Precision in this case can be expressed in terms of the relative standard deviation (RSD) as shown in Table 1. The RSD was below 15 % for concentration above 20 µg/l and less than 25% for concentration between 5 – 20 µg/l. This indicates reasonably good precision were obtained.

Specificity or Selectivity

Specificity is the ability to assess unequivocally the analyte in the presence of interferences, which may be expected to be present such as impurities, degradation products and matrix components, whereas other reputable international authorities (IUPAC, AOAC) have preferred the term selectivity, reserving specificity for those procedures that are completely selective [16].

The selectivity of the analytical method in this study was determined by comparing the results from the standard samples with the results obtained from spiked standard samples in the presence of other ions namely Cu(II), Ni(II), Fe(II), Zn(II), Cd(II), Mn(II) and Co(II) in the concentrations of five times than the concentration of Pb(II). Table 2 shows the percentages of the extraction of the spiked and non-spiked samples. Statistical analysis, ANOVA showed that there is no significant difference ($P > 0.05$) in the two sets of analytical results obtained.

Table 2 : Mean Recovery (%) of Extraction of Pb(II) with Tributyl Phosphate from standard samples and spiked standard samples in the presence of other ions.

Standard samples (mg/l)	Mean Recovery	%RSD	Spiked cations (mg/l)	Mean Recovery	% RSD
10	109	25.00	50	112	28.79
20	108	18.85	100	110	20.05
40	105	10.00	200	106	13.35
100	101	7.07	500	101	9.98

Method Detection Limit (MDL) and Limit of Quantitation (LOQ)

MDL is the lowest concentration of analyte in sample that can be detected but not necessarily quantified, under the stated conditions of the test [13]. LOQ, also known as the limit of reporting, is the lowest concentration of an analyte that can be determined with acceptable precision and accuracy under the stated conditions of test [14]. To determine the MDL, the water sample was spiked with freshly prepared Pb(II) standards at a concentration of 5 µg/l. It was then extraction with TBP at the optimum experimental conditions and determined by ICP-OES. The results are shown in Table 3. The MDL value was calculated from the standard deviations of ten replicates multiplied by the appropriate student's-t value for 99% confidence interval (3.707). The value found was 4.43 µg/l. Limit of Quantitation was defined as 3.33 times MDL thus in this case it is equal to 14.75 µg/l.

Table 3 : Method Detection Limit (MDL) for the Extraction of Pb(II) with TBP and Determined by ICP-OES

Samples	Concentration(mg/l)	Standard Deviation (SD)	RSD (%)
1	5.20	1.000	19.23
2	6.40	1.710	26.72
3	2.90	0.570	19.66
4	5.00	1.130	22.60
5	3.17	0.740	23.24
6	5.96	1.761	29.54
7	5.18	1.444	27.87
8	5.95	1.439	24.18
9	5.02	1.040	20.72
10	5.19	1.120	21.58
Mean	5.00	1.195	23.54

Robustness and Ruggedness

The robustness of an analytical procedure is a measure of its capacity to remain unaffected by small, but deliberate, variations in method parameters, and provides an indication of its reliability during normal usage [14]. Ruggedness test is a study of the behaviour of an analytical process when small changes in the environmental and/or operating conditions are made, to those likely to arise in different test environment. Ruggedness testing will allow information to be obtained on the effects of minor changes in a quick and systematic manner. In this method, variations of pH in the range of 9 – 11 did not effectively change the percentage of recoveries. Time of shaking in the range of 2 – 5 minutes did not vary the result significantly.

Reproducibility

Reproducibility as defined by ICH (1995) [18] represents the precision obtained between laboratories. As shown in Table 4, four aqueous standard samples were analysed by different operators. ANOVA test were used to analyse the results. It was found that there is no significant difference ($P > 0.05$) in the two sets of analytical results obtained.

Table 4 : Intra-Laboratory Extraction of Pb(II) with Tributyl Phosphate

Labarotary A Samples (mg/l)	Recovery	%RSD	Labarotary B Samples (mg/l)	Recovery	% RSD
10	109	25.00	10	115	25.65
20	108	18.85	20	107	22.79
40	102	10.00	40	104	14.85
100	101	7.07	100	100	7.98

Measurement uncertainty for test result

Measurement uncertainty is a parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand. Measurand is a physical parameter being quantified by measurement [13]. The parameter may be, for example, a standard deviation or the width of a confidence interval. It is understood that the result of the measurement was the best estimated of the value measured and that all components of uncertainty, including those arising from systematic effects, such as components associated with corrections and reference standards, contribute to the dispersion. In this experiment the parameter involve are calibration of ICP-OES, measurement of sample volume with pipette (V_1), dilution of sample in volumetric flask (V_2), measurement volume of TBP with pipette before extraction (V_3), measurement of volume of TBP in separator funnel after extraction (V_4), measurement volume of HNO_3 with pipette before stripping (V_5) and measurement volume of HNO_3 after separation by separator funnel (V_6).

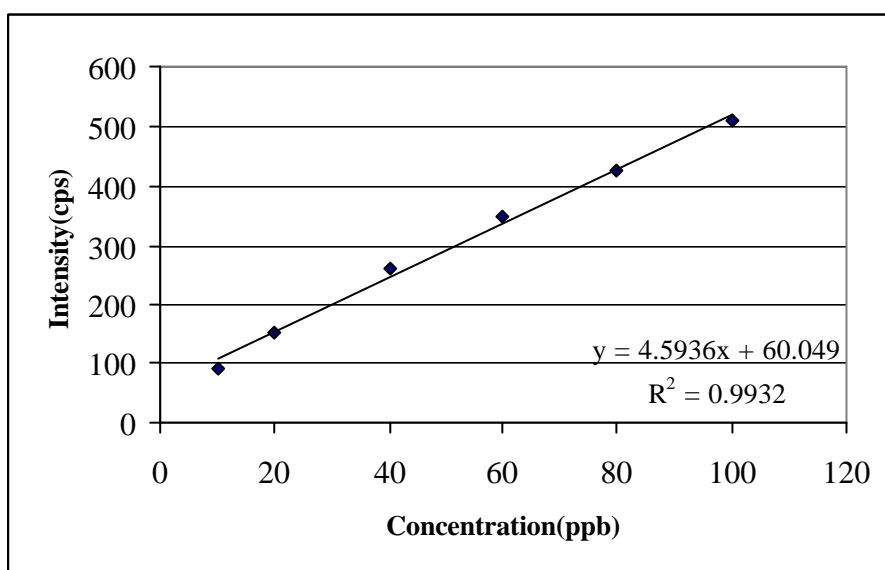


Figure 2 : Calibration graph for ICP-OES

The calibration of ICP-OES for Pb(II) concentration from 10 – 100 $\mu\text{g/l}$ as shown in Figure 2 was found to have the following characteristics:

$$y = 4.5936x + 60.049$$

Gradient, $m = 4.5936 \pm 0.0011$
 y-intercept, $c = 60.049 \pm 0.047$

Referring to the Figure 2, when the intensity of the Pb(II) is 198 cps, the concentration read from the calibration curve is $30.00 \pm 0.08 \mu\text{g/l}$. Table 5 shows all of the uncertainty sources and standard uncertainty $u(x)$ in the Pb(II) determination. Upon consideration of the complete procedure from sample preparation to instrumental determination as shown in Table 5, the expanded uncertainty for Pb(II) is found to be $0.143 \mu\text{g/l}$. Hence, a typical result of Pb^{2+} with uncertainty can be expressed as $30.00 \pm 0.14 \mu\text{g/l}$.

Table 5 : Uncertainty parameters in Pb(II) determination

Description	Value x	Standard uncertainty u (x)	Relative standard uncertainty u(x) / x
Concentration read from calibration (Pb ²⁺)	30.00 µg/l	0.08 µg/l	0.0064
Measurement of sample volume with pipette (V ₁)	10.00 ml	0.11 ml	0.011
Dilution of sample in volumetric flask (V ₂)	25.00 ml	0.10 ml	0.004
Measurement volume of TBP with pipette before extraction (V ₃)	1.00 ml	0.11 ml	0.110
Measurement of volume of TBP in separator funnel after extraction (V ₄)	1.00 ml	0.10 ml	0.100
Measurement volume of HNO ₃ with pipette before stripping (V ₅)	10.00 ml	0.11 ml	0.011
Measurement volume of HNO ₃ after separation by separator funnel(V ₆)	10.00 ml	0.10 ml	0.010

Nature of the extracted species

The nature of extracted species was determined by plotting log [D] against log [TBP] at fixed pH of 10.0, where [D] denoted the distribution ratio of Pb(II) between the two phases and [TBP] is the reagent concentration. The slope was 1.9. Therefore probable composition of the reaction species is

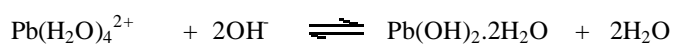
**Applications**

Table 6 shows the concentrations of dissolved Pb and Pb(II) at 6 stations along the Langat River. The dissolved fractions were obtained from the filtration of samples with 0.45 µm membrane filter followed by determination using ICP-OES. The concentration of Pb(II) in the dissolved fraction was then obtained by means of the TBP extraction method.

Table 6 : Extraction of Pb(II) from dissolved Pb fraction by tri-butyl phosphate

Station	Dissolved Pb (mg/l)	% RSD	Pb(II) extracted with TBP (mg/l)	% RSD	% Pb(II) in dissolved Pb fraction
1	6.74	17.91	5.36	22.06	79.53
2	7.31	10.82	4.66	21.23	63.75
3	11.50	15.87	8.90	12.70	77.40
4	4.62	19.73	3.30	25.53	71.43
5	5.54	12.41	4.34	20.25	78.34
6	30.90	8.43	22.97	13.25	74.34

From the Table 6, it is shown that the percentages of Pb(II), which include Pb(OH)^+ , Pb(OH)_2 and Pb(OH)_3^- [19] in the dissolved fraction was in a range of 64 - 80 %. This percentage of Pb(II) was compared with the calculated value by computer based on chemical equilibrium model, MINTEQA2. This model showed that the percentage of Pb(II) was in the range of 55-78%. Statistical analysis, ANOVA showed no significant different ($P>0.05$) of Pb(II) concentration from the both method.

Conclusions

At the optimal conditions the technique shows high accuracy and good linearity with a correlation coefficient of 0.9932 for the calibration curve. This method is very sensitive and has good precision with the MDL of 4.43 $\mu\text{g/l}$ and LOQ of 14.75 $\mu\text{g/l}$ and with the mean relative standard deviation (RSD) of less than 20%. Mean recovery of almost 100% was achieved. This method also shows moderate robustness and ruggedness. Application of the method to water samples from six stations of Langat River has shown that the percentages of Pb(II), which include Pb(OH)^+ , Pb(OH)_2 and Pb(OH)_3^- , in the dissolved fraction were in a range of 64 - 80 %. Statistical analysis, ANOVA showed no significant different ($P>0.05$) of Pb(II) concentration determined by the TBP extraction method against the results of calculation using the chemical equilibrium model, MINTEQA2.

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