APPENDIX A

CARBON PASTE ELECTRODE

Appendix A-2 The current from stripping voltammogram of 10 mg L^{-1} Cd(II) at unmodified electrode

Electrolyte	Current $\times 10^{-5}$(A)				SD	%RSD
	Replicat1	Replicat2	Replicat3	average		
0.2 HNO_3	0.000	0.000	0.000	0.000	0.000	-
0.2 M acetate buffer (pH5)	2.274	2.157	2.393	2.275	0.118	5.19
0.3 M ammonium acetate	7.429	7.414	7.556	7.466	0.078	1.04
0.2 M sodium acetate	5.935	6.167	5.852	5.985	0.163	2.73

Appendix A-1 The current from stripping voltammogram of 10 mg L^{-1} Cu(II) at unmodified electrode

Electrolyte	Current $\times 10^{-5}$(A)				SD	%RSD
	Replicat1	Replicat2	Replicat3	average		
0.2 HNO_3	0.000	0.000	0.000	0.000	0.000	-
0.2 M acetate buffer (pH5)	25.740	24.351	23.137	24.409	1.302	5.34
0.3 M ammonium acetate	0.000	0.000	0.000	0.000	0.000	-
0.2 M sodium acetate	15.589	16.784	16.143	16.172	0.598	3.70

Appendix A-3 The current from stripping voltammogram of 10 mg L^{-1} Hg(II) at unmodified electrode

Electrolyte	Current $\times 10^{-5}$(A)				SD	%RSD
	Replicat1	Replicat2	Replicat3	average		
0.2 HNO_3	0.000	0.000	0.000	0.000	0.000	-
0.2 M acetate buffer (pH5)	7.750	7.337	7.128	7.405	0.317	4.27
0.3 M ammonium acetate	0.000	0.000	0.000	0.000	0.000	-
0.2 M sodium acetate	2.949	2.851	3.130	2.977	0.142	4.76

Appendix A-4 The current from stripping voltammogram of 10 mg L^{-1} Pb(II) at unmodified electrode

Electrolyte	Current $\times 10^{-5}$(A)				SD	%RSD
	Replicat1	Replicat2	Replicat3	average		
0.2 HNO_3	84.285	83.432	86.730	84.816	1.712	2.02
0.2 M acetate buffer (pH5)	11.247	12.275	11.117	11.546	0.634	5.49
0.3 M ammonium acetate	4.573	4.680	4.447	4.567	0.117	2.55
0.2 M sodium acetate	13.420	12.287	13.183	12.963	0.598	4.61

Appendix A-5 The current from stripping voltammogram of 5 mg L^{-1}Cd(II) in 0.3 M CH_3COONH_4 at various group of xanthone compounds.

compound	Current × 10^{-5}(A)				SD	%RSD
	Replicat1	Replicat2	Replicat3	average		
unmodified	12.778	11.006	12.674	12.153	0.994	8.18
xanthone(7.5%w/w)	6.537	6.104	7.009	6.550	0.453	6.91
xanthone(15%w/w)	2.814	2.629	2.930	2.791	0.152	5.44
xanthene(7.5%w/w)	3.343	3.324	3.388	3.351	0.033	0.99
xanthene(15%w/w)	7.704	7.221	6.969	7.298	0.374	5.12
Thioxanthone(7.5%w/w)	7.001	7.465	7.474	7.313	0.270	3.69
Thioxanthone(15%w/w)	5.230	4.905	5.352	5.162	0.231	4.48
acridone(7.5%w/w)	7.046	7.597	7.964	7.536	0.462	6.13
acridone(15%w/w)	6.116	6.768	6.467	6.451	0.326	5.06

Appendix A-6 The current from stripping voltammogram of 5 mg L^{-1}Cu(II) in 0.2 M acetate buffer at various group of xanthone compounds.

compound	Current × 10^{-5}(A)				SD	%RSD
	Replicate1	Replicat2	Replicat3	average		
unmodified	9.648	9.556	9.077	9.427	0.307	3.25
xanthone(7.5%w/w)	2.929	2.905	2.636	2.823	0.163	5.77
xanthone(15%w/w)	2.401	2.097	2.260	2.253	0.152	6.75
xanthene(7.5%w/w)	4.206	4.026	4.662	4.298	0.328	7.63
xanthene(15%w/w)	1.609	1.508	1.725	1.614	0.109	6.73
Thioxanthone(7.5%w/w)	5.090	5.303	4.660	5.018	0.328	6.53
Thioxanthone(15%w/w)	2.891	2.725	2.541	2.719	0.175	6.44
acridone(7.5%w/w)	2.631	2.434	2.822	2.644	0.194	7.35
acridone(15%w/w)	2.133	2.294	2.272	2.233	0.087	3.91

Appendix A-7 The current from stripping voltammogram of 10 mg L^{-1}Hg(II) in 0.2 M acetate buffer at various group of xanthone compounds.

compound	Current × 10^{-5}(A)				SD	%RSD
	Replicate1	Replicat2	Replica3	average		
unmodified	4.231	4.268	4.529	4.343	0.162	3.73
xanthone(7.5%w/w)	4.058	4.087	4.050	4.065	0.020	0.48
xanthone(15%w/w)	3.599	3.448	3.448	3.498	0.087	2.50
xanthene(7.5%w/w)	1.905	1.904	1.755	1.854	0.086	4.66
xanthene(15%w/w)	1.621	1.703	1.516	1.613	0.094	5.82
Thioxanthone(7.5%w/w)	2.634	2.467	2.334	2.479	0.150	6.07
Thioxanthone(15%w/w)	1.745	1.644	1.620	1.669	0.066	3.98
acridone(7.5%w/w)	2.631	2.409	2.559	2.533	0.113	4.47
acridone(15%w/w)	2.250	2.413	2.393	2.352	0.089	3.77

Appendix A-8 The current from stripping voltammogram of 5 mg L^{-1}Pb(II) in 0.2 M HNO_3 at various group of xanthone compounds.

compound	Current × 10^{-5}(A)				SD	%RSD
	Replicate1	Replicat2	Replicat3	average		
unmodified	31.776	31.990	30.379	31.382	0.875	2.79
xanthone(7.5%w/w)	18.045	19.192	19.030	18.756	0.621	3.31
xanthone(15%w/w)	20.170	20.265	20.901	20.445	0.397	1.94
xanthene(7.5%w/w)	21.722	22.954	23.443	22.706	0.887	3.91
xanthene(15%w/w)	16.949	17.862	18.487	17.766	0.773	4.35
Thioxanthone(7.5%w/w)	14.177	13.069	13.176	13.474	0.611	4.54
Thioxanthone(15%w/w)	5.300	5.338	5.787	5.475	0.271	4.94
acridone(7.5%w/w)	19.969	19.334	19.238	19.514	0.397	2.04
acridone(15%w/w)	15.432	16.304	16.811	16.182	0.698	4.31

APPENDIX B

ADSORPTIVE STRIPPING VOLTAMMETRY CONDITION

Appendix B-1 The comparison of peak current between square wave and differential pulse of Pb(II) in 0.01 M ammonium acetate containing 10 μM 8-hydroxyquinoline at pH = 8.0

Square wave mode

Pb(II) Conc. ($\mu g\ L^{-1}$)	Current × 10^{-8}(A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
0	0.000	0.000	0.000	0.000	0.000	-
5	2.133	2.210	2.222	2.189	0.048	2.20
10	4.771	4.583	4.490	4.614	0.143	3.10
15	6.866	7.038	7.069	6.991	0.110	1.56
20	9.508	9.414	9.403	9.442	0.058	0.61

Differential pulse mode

Pb(II) Conc. ($\mu g\ L^{-1}$)	Current × 10^{-8}(A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
0	0.000	0.000	0.000	0.000	0.000	-
5	0.249	0.255	0.242	0.249	0.006	2.53
10	0.565	0.560	0.547	0.557	0.009	1.68
15	0.776	0.785	0.791	0.784	0.008	0.97
20	1.092	1.084	1.099	1.092	0.007	0.68

Appendix B-2 The comparison of peak height and peak area of Pb(II) in 0.01 M ammonium acetate containing 10 µM 8-hydroxyquinoline at pH = 8.0

Peak height

Pb(II) Conc. ($\mu g\ L^{-1}$)	Current × 10^{-8}(A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
0	0.000	0.000	0.000	0.000	0.000	-
5	2.133	2.210	2.222	2.189	0.048	2.21
10	4.771	4.583	4.490	4.614	0.143	3.10
15	6.866	7.038	7.069	6.991	0.110	1.57
20	9.508	9.414	9.403	9.442	0.058	0.61

Peak area

Pb(II) Conc. ($\mu g\ L^{-1}$)	Current × 10^{-8}(A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
0	0.000	0.000	0.000	0.000	0.000	-
5	0.110	0.111	0.111	0.111	0.001	0.80
10	0.268	0.257	0.242	0.256	0.013	5.18
15	0.387	0.396	0.400	0.394	0.007	1.65
20	0.583	0.576	0.572	0.577	0.006	1.01

Appendix B-3 Effects of supporting electrolyte on the peak current of 20 µg L^{-1} Pb(II) in the presence of 10 µM 8-hydroxyquinoline at pH = 8.0

Electrolyte	Current × 10^{-8}(A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
CH_3COONH_4	9.258	9.166	9.430	9.285	0.134	1.45
CH_3COONa	6.447	6.320	6.532	6.433	0.107	1.66
Tris	7.170	7.052	7.006	7.076	0.085	1.20
KNO_3	7.197	7.102	7.167	7.155	0.048	0.68
$NaNO_3$	6.792	6.814	6.430	6.679	0.216	3.23

Appendix B-4 Effects of electrolyte concentration on the peak current of 20 µg L^{-1} Pb(II) in the presence of 10 µM 8-hydroxyquinoline at pH = 8.0

CH_3COONH_4 Concentration (M)	Current × 10^{-8}(A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
0.01	8.772	8.540	8.751	8.687	0.128	1.475
0.05	8.867	8.526	8.820	8.738	0.185	2.114
0.1	9.947	9.787	9.891	9.875	0.081	0.822
0.2	8.603	8.574	8.615	8.597	0.021	0.247
0.3	8.297	8.251	8.152	8.233	0.074	0.902
0.4	7.488	7.509	7.548	7.515	0.031	0.407
0.5	7.164	7.172	7.559	7.298	0.226	3.092

Appendix B-5 Effects pH on the peak current of 20 μg L^{-1} Pb(II) in 0.1 M ammonium acetate containing 10 μM 8-hydroxyquinoline

pH	Current $\times 10^{-8}$ (A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
6.00	0.000	0.000	0.000	0.000	0.000	-
6.50	0.228	0.234	0.206	0.222	0.015	6.66
7.00	11.580	12.546	12.886	12.337	0.678	5.49
7.50	12.808	12.895	13.864	13.189	0.586	4.44
8.00	11.680	11.672	12.018	11.790	0.197	1.68
8.50	9.166	9.815	9.921	9.634	0.409	4.24
9.00	9.767	9.679	9.438	9.628	0.170	1.77
9.50	8.829	8.570	8.690	8.696	0.129	1.49
10.00	7.747	7.999	7.923	7.890	0.129	1.64

Appendix B-6 Effects of 8-hydroxyquinoline concentration on the peak current of 20 μg L^{-1} Pb(II) in 0.1 M ammonium acetate at pH = 7.5

8-hydroxyquinoline Concentration (μM)	Current $\times 10^{-8}$(A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
1	2.671	2.575	2.507	2.584	0.083	3.19
5	8.579	8.507	8.274	8.453	0.159	1.88
10	10.272	10.341	10.757	10.457	0.262	2.51
15	11.082	10.898	11.031	11.004	0.095	0.86
20	10.281	10.165	10.378	10.275	0.107	1.04
25	10.134	10.295	10.043	10.157	0.128	1.26
30	8.825	8.764	8.915	8.835	0.076	0.86
35	6.873	6.704	6.890	6.822	0.103	1.51
40	3.099	3.063	3.099	3.087	0.021	0.67

Appendix B-7 Effects of accumulation potential on the peak current of 20 μg L^{-1} Pb(II) in 0.1 M ammonium acetate containing 15 μM 8-hydroxyquinoline at pH = 7.5

Potential (V)	Current $\times 10^{-8}$(A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
-1.2	10.580	10.321	10.530	10.477	0.137	1.31
-1.1	11.423	11.530	11.449	11.467	0.056	0.49
-1.0	11.690	11.817	11.578	11.695	0.120	1.02
-0.9	11.789	11.603	11.448	11.613	0.171	1.47
-0.8	11.742	11.673	11.897	11.771	0.115	0.97
-0.7	11.686	11.831	11.597	11.705	0.118	1.01
-0.6	11.765	11.430	11.881	11.692	0.234	2.00
-0.5	11.804	11.725	11.624	11.718	0.090	0.77
-0.4	11.420	11.571	11.573	11.521	0.088	0.76
-0.3	11.012	11.025	11.264	11.100	0.142	1.28
-0.2	10.761	10.860	10.507	10.709	0.182	1.70

Appendix B-8 Effects of accumulation time on the peak current of 20 μg L^{-1} Pb(II) in 0.1 M ammonium acetate containing 15 μM 8-hydroxyquinoline at pH = 7.5

Time (s)	Current $\times 10^{-8}$(A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
30	6.1204	6.1307	5.9152	6.055	0.122	2.01
60	10.286	10.417	10.729	10.477	0.228	2.17
90	14.98	14.92	14.913	14.938	0.037	0.25
120	19.06	19.995	19.988	19.681	0.538	2.73
150	22.366	22.199	22.705	22.423	0.258	1.15
180	26.017	26.912	25.542	26.157	0.696	2.66
210	28.156	29.712	29.008	28.959	0.779	2.69
240	30.655	31.301	30.471	30.809	0.436	1.41
270	32.663	32.125	31.622	32.137	0.521	1.62
300	32.756	32.597	32.186	32.513	0.294	0.90
330	32.095	32.847	32.123	32.355	0.426	1.32
360	32.478	32.973	31.973	32.475	0.500	1.54

Appendix B-9 Effects of scan rate on the peak current of 20 μg L^{-1} Pb(II) in 0.1 M ammonium acetate containing 15 μM 8-hydroxyquinoline at pH = 7.5

Scan rate (V/s)	Current $\times 10^{-8}$(A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
0.1	18.492	19.104	17.654	18.417	0.728	3.95
0.2	22.828	24.599	22.525	23.317	1.120	4.80
0.3	26.811	25.306	26.680	26.266	0.834	3.17
0.4	31.191	30.399	30.211	30.600	0.520	1.70
0.5	32.058	33.842	32.315	32.738	0.964	2.95
0.6	34.728	33.011	33.404	33.714	0.900	2.67
0.7	35.905	35.287	35.692	35.628	0.314	0.88
0.8	36.567	36.107	36.545	36.406	0.259	0.71
0.9	37.897	38.866	38.397	38.387	0.485	1.26

Appendix B-10 Effects of pulse amplitude on the peak current of 20 μg L^{-1} Pb(II) in 0.1 M ammonium acetate containing 15 μM 8-hydroxyquinoline at pH = 7.5

Amplitude (mV)	Current $\times 10^{-8}$(A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
10	13.256	12.868	13.041	13.055	0.194	1.49
20	20.032	20.243	20.351	20.209	0.162	0.80
30	24.455	24.558	25.250	24.754	0.432	1.75
40	26.689	27.582	27.541	27.271	0.504	1.85
50	26.869	27.405	27.617	27.297	0.386	1.41

APPENDIX C

ANALYTICAL PERFORMANCES

Appendix C-1 The current of Pb(II) at the different concentration

Pb(II) conc. ($\mu g\ L^{-1}$)	Current $\times 10^{-8}$(A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
0.5	0.896	0.883	0.899	0.893	0.008	0.93
1	1.572	1.626	1.737	1.645	0.084	5.12
5	5.657	5.805	5.871	5.778	0.110	1.90
10	14.184	13.622	13.927	13.911	0.281	2.02
20	27.015	25.981	28.068	27.021	1.044	3.86
30	38.158	38.726	36.269	37.718	1.286	3.41
40	47.944	48.823	48.302	48.356	0.442	0.91
50	61.864	62.297	60.885	61.682	0.723	1.17
60	73.251	74.239	74.552	74.014	0.679	0.92
70	82.744	81.156	83.684	82.528	1.278	1.55
80	90.315	93.167	91.904	91.795	1.429	1.56
90	103.264	102.431	103.453	103.049	0.544	0.53
100	103.500	106.557	102.961	104.339	1.939	1.86
110	106.135	106.197	108.803	107.045	1.523	1.42
120	112.441	113.651	112.553	112.882	0.669	0.59

Appendix C-2 The comparison of current using calibration and standard addition method for Pb(II) determination in canned fish sample

Calibration

Pb(II) conc. ($\mu g\ L^{-1}$)	Current $\times 10^{-8}$(A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
0	0.000	0.000	0.000	0.000	0.000	0.00
2	3.191	3.528	3.377	3.365	0.168	5.01
4	7.481	7.652	7.551	7.561	0.086	1.14
6	11.676	11.859	11.300	11.612	0.285	2.45

Standard addition

Pb(II) conc. ($\mu g\ L^{-1}$)	Current $\times 10^{-8}$(A)				SD	%RSD
	Replicate 1	Replicate 2	Replicate 3	average		
0	0.381	0.391	0.363	0.379	0.014	3.67
2	2.332	2.363	2.577	2.424	0.133	5.50
4	5.013	5.164	5.194	5.124	0.097	1.89
6	7.429	7.457	7.975	7.621	0.307	4.03

Appendix C-3 The brand of canned fish samples

Sample no.	Brand
1	TCB
2	Pigeon
3	Hi-Q
4	Three Lady Cooks
5	Super C Chef
6	Sea Crown
7	Pum-Puy
8	Roza
9	Ayam
10	Blue Bird

Appendix C-4 Data for determination of Pb(II) in canned fish samples

Sample no.	Pb(II) concentration ($\mu g\ g^{-1}$)				SD	%RSD
	Replicate1	Replicate2	Replicate3	average		
1	0.177	0.149	0.152	0.160	0.015	9.62
2	0.267	0.288	0.299	0.285	0.016	5.75
3	0.222	0.205	0.196	0.208	0.013	6.32
4	0.196	0.187	0.156	0.180	0.021	11.61
5	0.253	0.300	0.224	0.259	0.038	14.79
6	0.158	0.130	0.164	0.151	0.018	11.95
7	0.157	0.141	0.122	0.140	0.018	12.51
8	0.252	0.299	0.243	0.265	0.030	11.30
9	0.119	0.116	0.128	0.121	0.006	5.23
10	0.243	0.296	0.291	0.277	0.029	10.62

Determination of Lead in Canned Food by Stripping Voltammetry

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Abstract

A sensitive and rapid method for analysis of Pb(II) in canned fish samples was developed using adsorptive cathodic stripping voltammetry technique. The method is based on the adsorptive accumulation of 8-hydroxyquinoline complexes of Pb(II) onto a hanging mercury drop electrode, followed by reduction of adsorbed species by voltammetric scan using square wave pulse modulation. The optimum experimental conditions and parameters were found to be 0.1 M CH_3COONH_4 as the supporting electrolyte, pH of 7.5, a 8-hydroxyquinoline concentration of 15 µM, accumulation potential at -0.7 V (vs. Ag/AgCl) accumulation time of 120 s, scan rate of 0.3 V/s and pulse amplitude of 20 mV. Under the optimum conditions the linear calibration graph was obtained in the concentration range 0.5 - 90.0 µg L^{-1} with correlation coefficient 0.9973, the limit of detection (LOD) is 0.108 µg L^{-1} and the limit of quantification (LOQ) is 0.360 µg L^{-1}. The recovery values were obtained in the range 93.68 - 95.13%. The relative standard deviation (n = 10) at lead concentrations of 1.0, 5.0 and 10.0 µg L^{-1} were 6.23%, 2.40% and 2.00% respectively. The studied method was successfully applied to the determination of lead content in a canned fish sample. The concentration of Pb(II) in canned fish samples (wet weight) were found in range 0.121 – 0.285 µg g^{-1}. However, the concentration of Pb(II) in canned fish samples were lower than the food contamination standard limited level (< 1.00 µg g^{-1}) issued by the Ministry of Public Health of Thailand.

Keywords: Lead, canned fish, adsorptive stripping voltammetry

1. Introduction

There is increasing concern about the quality of foods in several parts of world. The determination of toxic elements in food has prompted studies on toxicological effects of them in food [1]. Lead can enter food during harvesting, and the lead added in processing or packaging [2].

Fish is widely consumed in many parts of the world by humans because it has high protein content, low saturated fat and also contains omega fatty acids known to support good health. Canned fishes in particular are well eaten in the developed world because it is convenient and affordable for most working families [3]. So their toxic metal content should be of some concern to human health.

Fish may be contaminated by lead during fish growth, transportation, and storage. Contamination of lead may also occur during production handling and canning process [3]. Solder used in the manufacture of cans is a recognized source of contamination of food by lead during canning [4]. Lead is found at high concentration in muscles and organs of fish. It accumulates in the human body where it replaces calcium in bones [5].

There are several methods that can determine lead at trace levels such as graphite furnace atomic absorption spectrometry (GFAAS) [6], atomic emission spectrometry (AES) generally with inductively coupled plasma (ICP-AES) [7], inductively coupled plasma-mass spectrometry (ICP-MS) [8], neutron-activation analysis (NAA) [9] and X-ray fluorescence spectrometry [10]. However, these techniques have some disadvantages, such as complicated operation, high cost of maintenance, expensive apparatus and requiring well-controlled experimental conditions. (Hu *et.al.*, 2003).

Electroanalytical techniques specially stripping analysis are well known as excellent procedures for the determination of trace chemical species. The advantages of this techniques are low cost, high sensitivity, easy operation and the ability of analyzing element speciation [11].

Stripping analysis is generally recognized as one of the most suitable methods for trace metal determination. Its remarkable sensitivity is attributed to the combination of an effective preconcentration step with advanced measurement procedures that generate an extremely favorable signal-to-background ratio. Since the metals are preconcentrated into the electrode by factors of 100 to 1000 [12].

Adsorptive cathodic stripping voltammetry (AdCSV) is becoming increasingly popular for the determination of trace and ultratrace levels of metal ions [13]. The technique is based upon adsorptive accumulation of the metal ion complex with a suitable ligand at the electrode scanning in the negative direction [14]. In AdCSV, a ligand of M^{n+} is added to form a complex, which is preconcentrated by adsorption at the electrode surface [15]. The reduction step, with a negative-going potential scan or constant cathodic current, can be employed for measuring the adsorbed complex. The adsorptive accumulation approach results in a very effective preconcentration with short adsorption times (1–5 min) and extremely sensitive or selectivity trace metal measurements [12].

The sensitivity in AdCSV is often greater than in ASV, because the metal is not dissolved in the mercury, but rather forms a monomolecular complex layer on, e.g., a mercury film electrode surface. Most AdCSV procedures utilize the hanging mercury drop electrode (HMDE) for measuring reducible species, which offers the advantages of self-cleaning, reproducible surface area, and automatic control [16].

Because of the great sensitivity enhancement obtained with AdCSV methods, several complexing agents have been studied for the adsorptive collection of complexes with Pb(II) on the hanging mercury drop electrode (HMDE). It has been previously described the use of 8-hydroxyquinoline [17], Xylenol Orange [18], Calcein Blue [19], Morin [20] and Thymolphthalexone [21] as complexing agents for the voltammetric determination of lead.

8-Hydroxyquinoline (oxine) is a well known complexing agent for the analytical determination of cations of transition metals [22]. 8-Hydroxyquinoline molecules are adsorbed on mercury, and this property is used as a preconcentration step for labile and non-labile complexes in electroanalytical procedures [23].

In this work, a adsorptive cathodic stripping voltammetric technique was developed for trace measurement of lead. The method is based on the effective accumulation of the lead(II) complex with 8-hydroxyquinoline on a hanging mercury drop electrode, the adsorbed complex is then reduced.

2. Experimental

2.1 Apparatus

The voltammetric measurements were performed using AUTOLAB PGSTAT 100 combined with the GPES software, using a multi-mode electrode in the hanging mercury drop electrode (HMDE) mode as working electrode, a Ag/AgCl/3 M KCl as reference electrode and a Pt wire as auxiliary electrode. Solutions were stirred during the purging and deposition steps by a rotating PTFE rod. The electrode cell was equipped with a nitrogen purge tube to remove oxygen prior to sample analysis. Square wave voltammetry experiments were carried out with pulse amplitude 20 mV and a scan rate of 0.3 V s^{-1}

2.2 Reagents and solutions

All the reagents used were of Analytical Reagent grade and de-ionized water was used throughout. Glassware was rinsed with 10% (v/v) nitric acid for 48 h followed by thorough rinsing with de-ionized water. Stock standard solution of 1,000 µg L^{-1} Pb(II) was prepared by using 1,000 mg L^{-1} Pb(II) (SCP Science) standard solution and diluted for the corresponding stock solution. Stock solution of 10^{-2} M 8-hydroxyquinoline (Fluka) was prepared by dissolving 0.07258 g 8-hydroxyquinoline in 0.2 M HCl and then diluted with de-ionized water in 50-ml volumetric flask. The supporting electrolyte was 0.1 M ammonium acetate. Appropriate volumes of this solution were adjusted to pH 7.5 with ammonium hydroxide solution.

2.3 Sampling

Canned fish samples (mackerel in tomato sauce) of ten brands were purchased from Lotus supermarkets (sampling date 5 July 2007).

2.4 Sample preparation and digestion

After opening each canned fish sample, fish and tomato sauce, was homogenized thoroughly in a food blender. Homogenized sample 1.5 g (wet weight) was placed into beaker and 15 mL of nitric acid : perchloric acid : sulphuric acid mixture (25 + 25 + 1 v:v:v) was added. The beaker was covered using watch glass and heated on the hot plate at 150 ^{o}C until the solution was clear. The clear solution was allowed to cool, transferred into a 25 mL volumetric flask and diluted to the mark with deionised distilled water [5].

2.5 General procedure

The sample solution (10 ml), containing 15 µM 8-hydroxyquinoline and 0.1 M CH_3COONH_4 (pH = 7.5) was pipetted into the voltammetric cell. The stirrer was switched on and the solution was purged with nitrogen gas for 1 min. After forming a new HMDE, accumulation was affected for 120 s at -0.7 V whilst stirring the solution. At the end of accumulation time, the stirrer was switched off, and after 10 s had elapsed to allow the solution to become quiescent, the voltammogram was recorded by applying a negative-going differential pulse scan.

3 Results and discussion

3.1 Adsorptive characteristics of the Pb-8-hydroxy-quinoline complex

Preliminary experiments were performed to characterize the suitability of 8-hydroxyquinoline for the determination of lead ion using HMDE. Fig. 1(a) displays stripping voltammogram of 0.1 mM 8-hydroxyquinoline solution in 0.01 M ammonium acetate at pH = 8.0 after 1 min accumulation at -0.4 V. Fig. 1(b) shows the stripping voltammogram of solution containing 1 mg L^{-1} Pb(II) in the absence of 8-hydroxyquinoline ligand under condition similar to those in Fig. 1(a). Fig. 1(c) shows the stripping voltammogram of mixture of 0.1 mM 8-hydroxyquinoline and 1 mg L^{-1} Pb(II) in 0.01 M ammonium acetate at pH = 8.0 after 1 min accumulation at -0.4 V. It had found reduction peak at -0.578 V (Fig. 1(c)). It can be concluded that the sensitivity of lead reduction currents enhanced due to the addition of 8-hydroxyquinoline to the solution. Indicate that the Pb-8-hydroxyquinoline complex was absorbed on the surface of electrode.

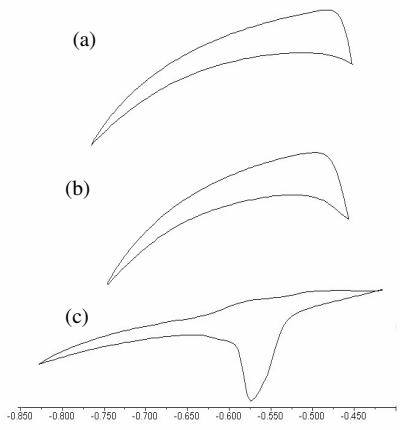

Fig. 1 Stripping voltammogram of (a) 0.1 mM 8-hydroxyquinoline (b) 1 mg L^{-1} Pb(II) (c) mixture of 0.1 mM 8-hydroxyquinoline and 1 mg L^{-1} Pb(II) in 0.01 M ammonium acetate at pH = 8.0 after 1 min accumulation at -0.4 V and scan rate of 50 mV s^{-1}

3.2 Comparison of square wave versus differential pulse

A number of different wave forms have been used for the stripping step, including linear sweep voltammetry (LSV), differential pulse voltammetry (DPV), and square wave voltammetry (SWV). SWV and DPV are more commonly used, due to their lower detection limits [15].

A comparison of the sensitivities for lead analysis between square wave and differential pulse is shown in Fig. 2. It was found that the sensitivity of square wave was higher than differential pulse. Thus, square wave was selected for all experiments.

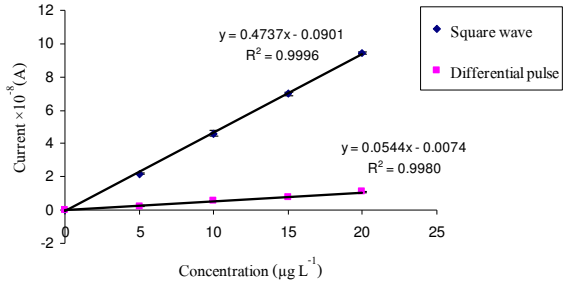

Fig. 2 The comparison of peak current between square wave and differential pulse of Pb(II) in 0.01 M ammonium acetate containing 10 µM 8-hydroxyquinoline at pH = 8.0

3.3 Effect of supporting electrolyte

Electrochemical measurements are commonly carried out in a medium that consists of a supporting electrolyte. Supporting electrolytes are required in controlled-potential experiments to decrease the resistance of the solution, and to maintain a constant ionic strength [12]. The effect of difference supporting electrolyte in 0.01 M of CH_3COONH_4, CH_3COONa, Tris, KNO_3 and $NaNO_3$ is shown in Fig. 3. The highest peak height was achieved in CH_3COONH_4 solution. Thus, CH_3COONH_4 was used as supporting electrolyte for further experiments.

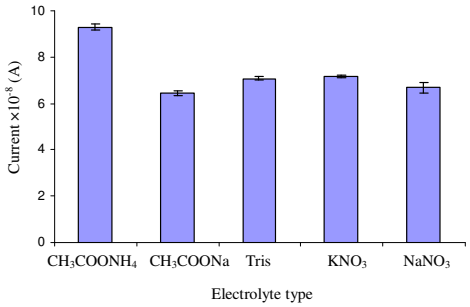

Fig. 3 Effects of supporting electrolyte on the peak current of 20 µg L^{-1} Pb(II) in the presence of 10 µM 8-hydroxyquinoline at pH = 8.0

3.4 Effect of supporting electrolyte concentration

The effect of concentration of the supporting electrolyte on the stripping peak current of Pb(II) was studied by varying the concentration of ammonium acetate in the range 0.01-0.5 M (Fig. 4). The maximum peak current was observed for 0.1 M ammonium acetate. It was found that increasing the concentration of ammonium acetate decreased the peak current. This is due the formation of a weak complex between acetate with Pb(II) [24]**.** Consequently an optimum ammonium acetate concentration of 0.1M was selected for the next experiments.

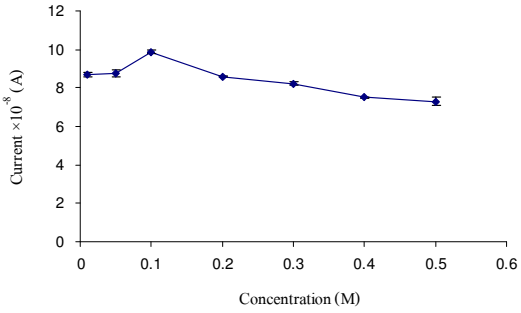

Fig. 4 Effects of electrolyte concentration on the peak current of 20 µg L^{-1} Pb(II) in the presence of 10 µM 8-hydroxyquinoline at pH = 8.0

3.5 Effect of pH

The influence of pH on the stripping peak current of Pb(II) was studied in the pH range 6.00 - 7.00. The results are shown in Fig. 5 indicate that with a pH range of 6.00 to 7.50 the peak current of the lead complex increased by increasing pH and then decreased by changing pH from 8.00 to 10.00. Thus a pH of 7.50 was chosen for further studies.

At very low pH, the protonation of -NH groups (in 8-hydroxyquinoline) [25] and at high pH, hydrolysis of Pb(II) which would increasingly affect the formation of Pb(II)-8-hydroxyquinoline complexes [26]. Therefore, at low and high pH the complexation of 8-hydroxyquinoline with Pb(II) ions will decrease.

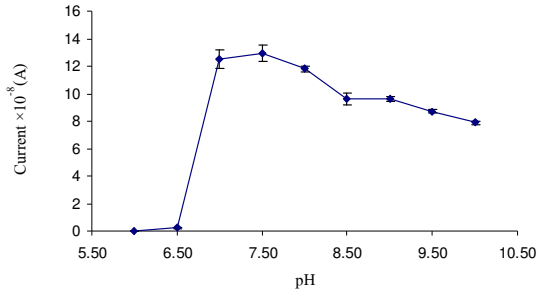

Fig. 5 Effects pH on the peak current of 20 µg L^{-1} Pb(II) in 0.1 M ammonium acetate containing 10 µM 8-hydroxyquinoline

3.6 Effect of 8-hydroxyquinoline concentration

The effect of the 8-hydroxyquinoline concentration on the cathodic stripping peak current of 20 µg L^{-1} Pb(II) in 0.1 M ammonium acetate at pH 7.5 with a accumulation potential of -1.1 V for 60 s is shown in Fig 6. The effect of 8-hydroxyquinoline concentration is shown that the stripping peak current for Pb(II) increased up to 15 M and in higher 8-hydroxyquinoline concentration the peak current heights decreased due to the competition of 8-hydroxyquinoline with Pb(II)-8-hydroxyquinoline complexes for adsorption onto the mercury drop electrode [14]. Therefore, the 8-hydroxyquinoline concentration of 15 µM was selected as optimum value for further experiments.

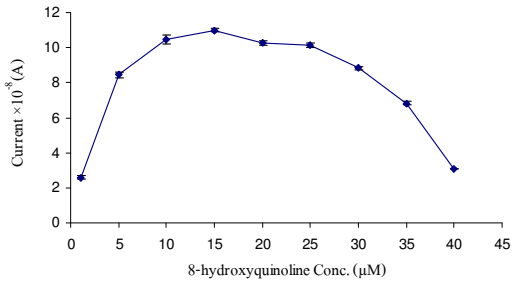

Fig 6 Effects of 8-hydroxyquinoline concentration on the peak current of 20 µg L^{-1} Pb(II) in 0.1 M ammonium acetate at pH = 7.5

3.7 Effect of accumulation potential

The effect of varying accumulation potential on the peak current for Pb(II) determination is shown in Fig 7. The accumulation potential was varied between -1.2 and -0.2 V. The obtained results shown that that the peak current of Pb(II) was found constant between -0.8 V to -0.5 V. Thus, an accumulation potential of -0.7 V was selected for lead accumulation because the peak current at -0.7 V shown constant current and better sensitivity.

3.8 Effect of accumulation time

The effect of varying accumulation time on the peak current for Pb(II) determination is shown in Fig. 8. It was found that the peak current of Pb(II) increased linearly with the accumulation time, gradually levelling off at periods longer than 270 s is presumably due to saturation of the HMDE surface at longer accumulation time [27]. Thus, an adsorption time of 120 s was used throughout this work as it combines good sensitivity with relatively short analysis time.

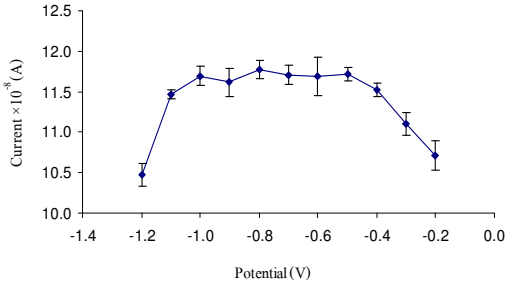

Fig. 7 Effects of accumulation potential on the peak current of 20 µg L^{-1} Pb(II) in 0.1 M ammonium acetate containing 15 µM 8-hydroxyquinoline at pH = 7.5

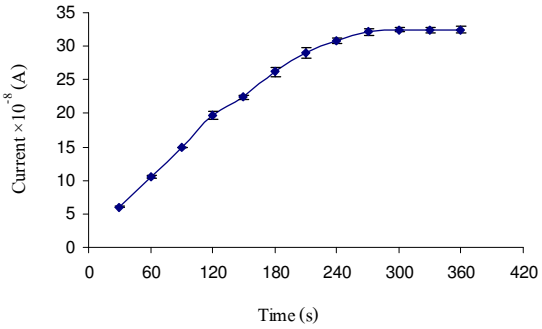

Fig. 8 Effects of accumulation time on the peak current of 20 µg L^{-1} Pb(II) in 0.1 M ammonium acetate containing 15 µM 8-hydroxyquinoline at pH = 7.5

3.9 Effect of scan rate and pulse amplitude

To improve the sensitivity for the determination of Pb(II), the influences of parameters of square wave voltammetry on the measurement of lead were studied. The effect of step potential and pulse amplitude on the peak current is shown Fig. 9- 10

The dependence of peak currents on the scan rate step potential and pulse amplitude under the optimal conditions was also investigated in the range of 0.1 – 0.9 V/s and 10 - 50 mV. The peak current for lead increased with increasing scan rate and pulse amplitude. Therefore, a scan rate of 0.3 V/s and pulse amplitude 20 mV were selected because of the better sensitivity and peak shape.

3.10 Analytical performances

At the optimized conditions, the linear calibration graph was obtained in the concentration range 0.5 - 90.0 µg L^{-1} with correlation coefficient 0.9973.

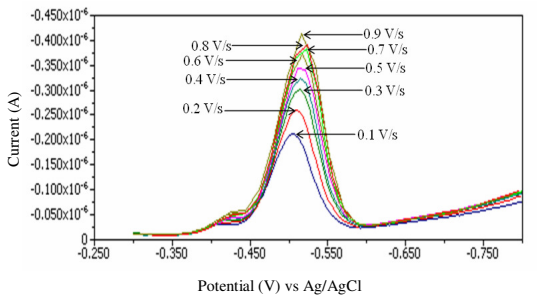

Fig. 9 Voltammograms of varied scan rates on the peak current of 20 µg L^{-1} Pb(II) in 0.1 M ammonium acetate containing 15 µM 8-hydroxyquinoline at pH=7.5

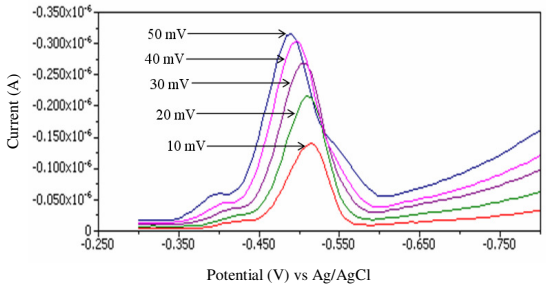

Fig. 10 Voltammograms of varied pulse amplitude on the peak current of 20 µg L^{-1} Pb(II) in 0.1 M ammonium acetate containing 15 µM 8-hydroxyquinoline at pH = 7.5

The limit of detection (LOD) and the limit of quantification (LOQ) were calculated by carrying out the above procedure on 10 blank samples using the equation

$$LOD = (3*SD)/m$$
$$LOQ = (10*SD)/m$$

When, SD = standard deviation of blank
m = slope of calibration graph

The limit of detection was 0.108 µg L^{-1} and the limit of quantification was 0.360 µg L^{-1}.

The accuracy of the concentrations determined in this study was checked by spiking the canned fish samples before sample was digestion with various concentration of Pb(II) for the percent recovery. The result is shown in Table 1. The percent recovery values were obtained in the range 93.68 - 95.13%.

The analytical precision of the method was estimated from the reproducibility of 10 determinations at several lead concentrations; the relative standard deviation at lead concentrations of 1.0, 5.0 and 10.0 µg L^{-1} were 6.23%, 2.40% and 2.00% respectively.

Table 1 The percent recovery of Pb(II) at concentration of 10, 20 and 30 µg L^{-1} in canned fish

Experment	Pb(II) concentration (µg L^{-1})	%Recovery
sample	9.582	-
sample + 10 ug/L	18.984	94.02
sample + 20 ug/L	28.318	93.68
sample + 30 ug/L	38.121	95.13

3.11 Interferences

Possible interference by other metals with the adsorptive cathodic stripping voltammetry determination of Pb(II) was investigated by the addition of the interfering ion to a solution containing 20.0 µg L^{-1} of Pb(II) and carrying out the measurements at the optimized conditions. The results of this study are summarized in Table 2.

Table 2 Change in peak current of 20 µg L^{-1} Pb(II) in the presence of other ions

Metal Interferences	Concentration (µg L^{-1})	Change in peak current (%)
Fe^{2+}	100	-0.3
Mn^{2+}	100	7.7
Cr^{3+}	100	4.3
Hg^{2+}	100	-1.4
Sn^{2+}	60	-10.8
Cd^{2+}	20	-13.7
Zn^{2+}	20	-8.2
Al^{3+}	20	-12.9
Cu^{2+}	20	-32.9
Ni^{2+}	20	-29.5

From the result, it can be concluded that several ions such as Fe^{2+}, Cr^{3+}, Mn^{2+} and Hg^{2+} (5-fold concentration); Sn^{2+} (3-fold concentration); Cd^{2+}, Zn^{2+}, and Al^{3+} (equal concentration); have only negligible effect on the determination Pb^{2+}. However, equal concentration amount of Cu^{2+} and Ni^{2+} interfere significantly by decreasing the Pb^{2+} signal, but the peak of Pb^{2+} is still well separated from all of them.

3.12 Application

The proposed method was applied to the determination of Pb(II) in canned fish samples. The standard addition method was used, in order to eliminate the matrix effect. The results are shown in Table 3.

Table 3 Pb(II) concentration in canned fish samples by standard addition method

Sample no.	Pb concentration (µg g^{-1}) (wet weight)
1	0.160
2	0.285
3	0.208
4	0.180
5	0.259
6	0.151
7	0.140
8	0.265
9	0.121
10	0.277

The concentration of Pb(II) in canned fish samples (wet weight) were found in range 0.121 – 0.285 μg g^{-1}. However, the concentration of Pb(II) in canned fish samples were lower than the food contamination standard limited level (< 1.00 μg g^{-1}) issued by the Ministry of Public Health of Thailand.

4. Conclusion

The present study demonstrates that adsorptive cathodic stripping voltammetry of lead based on accumulation of Pb(II)- 8-hydroxyquinoline complex can be used to determine trace amounts of lead in canned fish samples. This method has simple, sensitive, inexpensive and rapid for the determination of Pb(II).

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