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The use of stripping voltammetry for lead determination during toxic chemicals detoxication by an electrochemical method

Volgina Tatyana N.^{a,*}, Katyuhin Vladimir E.^a

^aNational Research Tomsk Polytechnic University, 30 Lenina av., Tomsk, 634050, Russia

Abstract

The paper describes the results of stripping voltammetry usage to control concentration of lead ion which are formed during electrochemical detoxication of organic pollutants. Optimal conditions for the analysis of Pb^{2+} were selected, i.e. 0.05 N KOH is an electrolyte, the deposition potential (-0.55) V, deposition time of 4 minutes, the amount of analyzed sample was 0.1 ml. The presence of organic matter does not affect the quantitative determination of lead ions. The developed method allows us to estimate the concentration of Pb^{2+} in the amount of electrolyte at disposal of toxicants quickly and with a high degree of sensitivity.

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1. Introduction

Metals are of priority interest among numerous chemical substances, which pollute objects of the environment. They are extremely dangerous for the proper functioning of ecosystems, because once they are in the biochemical cycle, they desolate it rather slowly. One of such elements is lead that is superecotoxicant, which influences biochemical processes in a cell and causes cancerogenic and mutagenic effects.

Stripping voltammetry (SV) is widely used of all the existing physicochemical methods of controlling lead on the level of maximum permissible concentration in various objects. In some cases this method is ideal for determination of trace amounts of metal¹.

* Corresponding author. Tel.: +7-382-260-6120

E-mail address: volgina_t@mail.ru

However, there is no common method to determine lead, which could be applied for analysis of any objects. The influence of various factors to consider, for example, the composition of electrolyte, the presence of organic compounds or other metals, pH level of the sample, often requires a special approach to the development of a specific analytical procedure.

The aim of this work is to determine optimal conditions for the detection of lead transferred into a solution and precipitated from the surface of lead electrodes during detoxication of organic toxicants by an electrochemical method in sulfurous medium.

Nomenclature

UV	ultraviolet radiation
PU	the universal polarograph
CD	current density
SV	stripping voltammetry
VC	voltammetric curve

2. Experiment

The development of analytical procedure for determining lead was carried out on polarograph PU-1. Voltammetric curves were received in the regime of linear anode change of the potential of working electrode, i.e. mercury film electrode, at the rate of 25-40 mV/sec, the electrode for comparison was silver-chloride. Stirring of the solution was carried out using a magnetic stir bar. UV-irradiation (UV) of 5 ml samples was conducted using a mercury quartz lamp for 5 minutes. All quartz beakers were calcinated before the procedures in an incinerator at 500 °C.

The method was tested using the samples collected during oxidation of phenol, which was taken as a model compound, i.e. a toxicant. Electrooxidation was conducted with current density of 0.1–1 A/cm². The electrolyte was 40 % water solution of sulfuric acid (70 ml). The process lasted for 80 minutes with initial phenol concentration of 1 g/l.

3. Results and discussion

Detoxication of phenol goes under the oxidation system formed when a flow of direct current passes through water solutions of sulfuric acid², where a negative electrode is lead, a positive electrode is PbO₂, being one of the most effective and available in mineralizing of organic substances³. When the working values of current density (CD) are 0.5 A/cm² and higher, there is electrode destruction. This leads to electrolyte contamination with toxic lead in the form of Pb²⁺ and PbSO₄. After detoxication the amount of lead in a liquid phase will determine the category of waste or the class of hazard to which the used electrolyte refers.

In advance it was experimentally determined by a colorimetric method that the ions of lead appear in the electrolyte in the first minutes of the process as a result of electrolysis of sulfuric acid with CD of 0.5-1 A/cm². On average when electrolysis goes on for 15 minutes, its concentration is in the range of 20 to 40 mg/l. This level is significantly higher than the maximum permissible norms that should be 0.2-1 mg/l for wastewater of industrial plants in the Russian Federation and the European Union.

In order to observe the dynamics of lead accumulation in electrolyte during detoxication of toxicants it is necessary to develop an express method to determine trace amounts of Pb. The optimal method of reaching this goal is SV, where the current of metal oxidation from amalgam reduced electrochemically on the cathode in the preliminary stages of accumulation is used as an analytical signal.

The development of method of Pb²⁺ determination in the specified conditions was carried out by stages. Firstly, an electrolyte was chosen. Then the potential of working electrode at the stage of preliminary electrochemical accumulation and in the conditions of sample preparation for the analysis were determined.

It is known that ions of lead are determined by stripping voltammetry on many electrolytes⁴. Under the conditions of this experiment, it is important to select an electrolyte, which allows us to conduct adequate quantitative assessment of lead ions without carrying out the preliminary phase of neutralization of sulfuric sample. We chose 0.05 M KOH as electrolyte; its pH level and the potential of anode peak of the current of metal oxidation from amalgam virtually do not change when a sulfurous sample is added into the electrolyte during the analysis. Below there is an example that describes this dependence.

Table 1. Correlation of the height of anode peak of lead with the concentration of potassium hydroxide.

Concentration KOH (mol/l)	Peak height (mm)
0.001	22.33
0.05	30.00
0.1	23.33
0.2	6.67

The sample, which we selected experimentally, is 0.1-1 ml and contains from 2 to 20 mg of lead ions. When the sample is more than 1 ml, the offset potential occurs due to the change of pH level of the electrolyte. When the sample is less than 0.1 ml, the response is the same as the electrolyte voltammetric curve (VC).

The determination of the value of electrode potential at the stage of preliminary electrolysis has shown that lead emission is at its maximum and there is no interference of other ions when the potential of maximum current is (-0.55) V towards a silver-chloride electrode. An accumulation period under the conditions of the test did not exceed 4 minutes. After concentration, anode oxidation of metal amalgam occurs; which results in the peak registered on the VC. See Fig.1 as an example. This also allows us to conduct quantitative assessment of the content of lead ions.

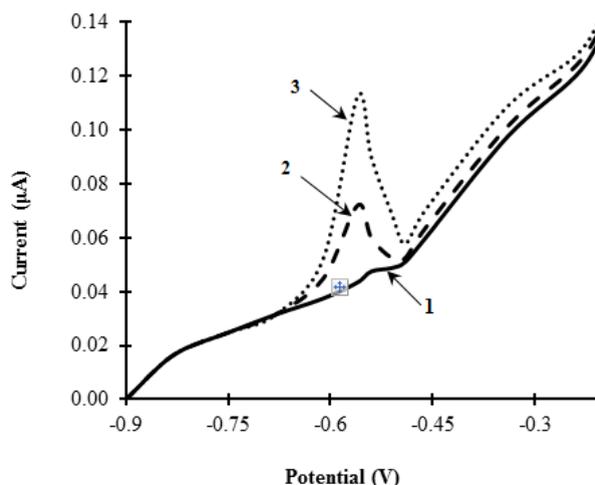


Fig. 1. Anode voltammetric curve of lead: 1 – curve acquired in electrolyte solution before the analyzed sample was introduced, 2 – after the sample was introduced, 3 – after the introduction of standard solution.

The correlation of the anode peak height and the lead concentration in the solution is a straight line from the origin of coordinates in the selected background when the potential is constant and an accumulation period is optimal. As the experiments have shown, this correlation remains in the range of large concentrations of the determined element (up to 100 mg/dm³). This allows us to use the standard addition method to determine the quantity of Pb²⁺ by a stripping voltammetry.

The average value of the variations obtained during the analysis of 10 samples with Pb²⁺ concentrations of 0.4 and 0.8 mmol/l was 0.04 and 0.1 mmol/l respectively. The obtained value differs from the real content of lead in the analyzed solution by no more than 10 %. Thus, the selected optimal conditions of express-analysis of lead (Table 2)

allow us to determine the concentration of Pb^{2+} in sulfurous solutions at the level of maximum permissible concentrations for wastewater of industrial plants. Below there is an example which presents the optimal conditions.

Table 2. Conditions of stripping voltammetry determination of lead ions.

Parameter	Value
Electrolyte	0.05 and KOH
Potential	-0.55 V
Time accumulation	4 min
Electrolyte volume	5 ml
Concentration of the standard solution	50 mg/l
Sample volume	0.1 ml

The developed method was used to determine Pb^{2+} in the samples, which were taken during the detoxication process of phenol solutions. The analysis has shown that the amount of lead in the electrolyte at 40th minute of the process is at its maximum and equals 10-12 mg.

As the duration of electrooxidation increases, this value remains the same because some part of Pb^{2+} ions from the interaction with sulfate ions formed during the electrolysis of sulfuric acid form low-soluble residual of $PbSO_4$. It is determined by the data of infrared spectroscopy.

During the experiments, it was determined that the residual content of phenol and the products of its oxidation influence the quantitative assessment of lead ions. With organic fragments the form of anode metal peaks distorts which complicates their interpretation. To eliminate this interference, the analyzed sample was subjected to UV-irradiation for 15 minutes before the analysis. Below is an example which shows the effect of organic matter on the reliability of metal identification.

Table 3. Correlation of lead concentration and time of phenol detoxication.

Time (min)	Concentration Pb^{2+} (mg/l)	
	without UV-irradiation	with UV-irradiation
40	147	174
80	139	145

Therefore, the presence of organic substances is not desirable in the case of quantitative determination of lead.

4. Conclusion

The possibility of using of stripping voltammetry was shown and the conditions for quantitative determination of lead during the electrochemical disposal of toxicants were chosen.

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