

Determination of Lead by Square Wave Adsorptive Stripping Voltammetry Using Ammonium Pyrrolidine Dithiocarbamate

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Abstract: In this work optimal working conditions were established for the determination of trace levels of lead on hanging mercury drop electrode with Ammonium pyrrolidine dithiocarbamate (APDC) as a preconcentrating agent in acetate buffer media using square wave anodic stripping voltammetry. The optimized experimental conditions include pH, APDC concentration, accumulation time, accumulation potential, scan rate, pulse amplitude and SW frequency on the voltammetric response were studied. A linear relationship between the peak current and lead concentration was obtained over the range (5-40 ppb) with correlation coefficient of 0.99911. Detection limits of 0.89 ppb was obtained with standard deviation of 0.03706. The interference by metal ions which are of great significance in real matrices have been studied. The formation of complex formed between lead and APDC was investigated using both of SWASV and cyclic voltammetry technique. The method was successfully applied for the determination of lead in tap water samples.

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Key Words: Lead, APDC, Square wave, Cyclic Voltammetry, tap water

1. Introduction:

Lead is a ubiquitous environmental pollutant with no known biological function. It exhibits severe deleterious effect on human [1] that has strong chemical toxicity at low concentrations. It can occur as a result of industrialization in the production of pigments, anticorrosion coatings, lead smelter, alloys, and batteries, causing significant disturbances in air, dust, soil, water, sediments, food, etc. The world health organization (WHO) and the US environmental protection Agency (EPA) have set maximum levels of 50 and 10 $\mu\text{g l}^{-1}$ of Pb in sea water and drinking water, respectively [2,3]. Exposure to high levels of trace metal ions (e.g. Cd(II), Pb(II), Cu(II), and Hg(II)) causes a variety of health problems, because they tend to accumulate in the body, and have low rate of clearance [4,5]. Therefore, it is critical to minimize the exposure of humans to these contaminants and this can be ensured through effective water quality monitoring.

As we all know lead is one of the most abundant heavy metals and its toxic effects cause environmental and health problems because of its stability in contaminated sites and complexity of mechanism in biological toxicity, particularly dangerous for children leading to mental retardation when exist with abnormal concentration in body fluid [6]. Lead ions can also interfere directly with calcium signaling, since it has a similar ionic radius to Ca^{2+} and hence the ability to substitute for calcium [7].

Several analytical techniques are available for quantification of lead such as atomic absorption spectrometry (AAS) [8], inductive coupled plasma mass spectrometry (ICP-MS) [9], inductive coupled plasma atomic emission spectrometry (ICP-AES) [10], high performance liquid chromatography [11], capillary electrophoresis [12], backward line scattering [13], and anodic stripping voltammetry (ASV) [14]. Among these methods, adsorptive stripping voltammetry (AdSV) is commonly employed because of its wide linear dynamic range and low detection limit which achieved as the result of performing the preconcentration steps directly into the voltammetric cell, thus decreasing the sampling handling, risk of sample contamination, and multi-element analysis capacity. An additional advantage of AdSV over other methods is the simplicity of the instrumentation, which is relatively inexpensive, small in size, requires low levels of electrical power and is sufficiently portable to permit its use in the field. Also possibility of analyzing various samples without the need of a prior separation is also convenient. Thus, adsorptive stripping analysis [15-17] is becoming a widely accepted tool for trace amount measurements of heavy metal ions. The history, theoretical background and application, of AdSV are given in references [18-21]. AdSV is widely used for individual and simultaneous determination of heavy metals and many reports on the application of AdSV for the determination of lead were listed [22-25]. The mercury film electrode (MFE)

[14] and the hanging mercury electrode (HMDE) [26] have been traditionally used for ASV because of the advantageous analytical properties of mercury in the negative potential range. So the aim of this work is to find a new procedure to determine the concentration of the lead using a APDC on HMDE using anodic stripping voltammetry .

2. Experimental:

2.1. Apparatus:

A Metrohm 693 VA processor with a three electrode system consisting of a hanging mercury drop electrode (HMDE) as the working electrode, Ag/AgCl reference electrode and a platinum counter electrode were used to obtain the voltammograms. A hanna 211 pH meter was used to determine the pH of solutions.

2.2. Reagents:

Ammonium pyrrolidine dithiocarbamate (Analar, BDH) was dissolved in absolute ethanol give 10^{-2} M stock solution. Stocks solution of lead (1000 mg l^{-1}) was prepared by dissolving 0.1598g of lead nitrate in deionized water and diluting to 100 ml in volumetric flask. Standard solutions of Pb(II) or ligand with lower concentrations were prepared daily by diluting the stock solutions. Acetate buffer was prepared by dissolving 13.6g of sodium acetatetrihydrate in deionized water and diluting to 1.0 L. Appropriate volumes of this solution were adjusted to the required pH with glacial acetic acid.

2.3. Procedure:

The general procedure adopted for obtaining square wave adsorptive stripping voltammograms was as follow:

The supporting electrolyte solution (10ml acetate buffer pH 3.5) containing $3 \mu\text{mol/L}$ was pipette into the cell and purged with nitrogen for 7 min. the deposition potential (-0.35V vs. Ag/AgCl) was applied to fresh mercury drop while the solution was stirred for 180sec. At the end of deposition time the stirrer was switched off, and after 10 sec had elapsed to allow the solution to become quiescent, the potential was scanned in a positive direction from -0.3 to 0 V using square wave adsorptive stripping Voltammetry, with a scan rate of 60 mV/sec. , Modulation frequency 160 Hz and a pulse amplitude of 50mV each scan was repeated three times with a new drop for each analyzed solution and the mean value was obtained.

After back ground stripping voltammograms had been obtained, an aliquot at the Pb(II) standard was introduced into the cell and following the described procedure, the sample voltammogram was achieved, lead peak was registered at about -0.35V ,

and its current was used as a measure of lead concentration all equipments were carried out at room temperature.

3-Results and Discussion

3.1 Effect of operational parameters:

3.1.1. Effect of pH variation:

The effect of the solutions pH on peak current (Fig. 1) of the Pb-APDC complex was studied in the $3.0 - 6.0$ range. C_{pb} and C_{APDC} were 20 ppb and $3.1 \mu\text{mol l}^{-1}$, respectively ($E_{\text{acc}}:-0.45\text{V}$, $t_{\text{acc}}:60\text{s}$). It is clear that peak current of the Pb-APDC complex is maximum at $\text{pH} = 3.5$ and decreases rapidly after $\text{pH} 3.7$. Greater pH values cause a decrease in the peak current and the signal is very broad probably due to the diminished complexing ability of the ligand at such pH values, so pH value of 3.5 was chosen for the whole study.

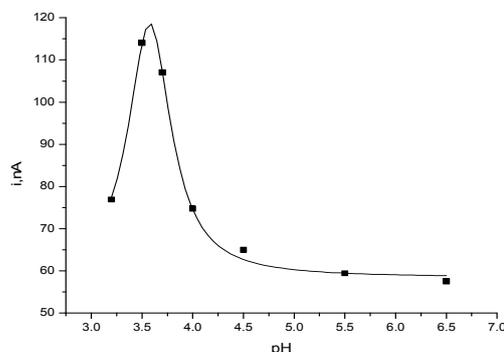


Fig.1: Influence of pH on the peak current of the Pb-APDC complex. Conditions: Pb(II): 25ng/ml ; $C_{\text{APDC}} : 3 \mu\text{M}$; $E_{\text{acc}}:-0.45\text{V}$; $t_{\text{acc}}:60\text{s}$; scan rate 20mV/s ; pulse amplitude : 20mV ; and frequency: 50Hz .

3.1.2. Effect of APDC concentration (C_{APDC}):

The influence of the ligand concentration on the peak current (Fig.2) was studied with APDC concentration in the range of ($0.1 \mu\text{mol l}^{-1} - 4.4 \mu\text{mol l}^{-1}$) for pb(II) 20 ng/ml , while other standard measuring conditions remained constant ($\text{pH} : 3.5$; $t_{\text{acc}} :60\text{s}$; $E_{\text{acc}}-0.45\text{v}$)

The results show that by increasing the ligand concentration the peak current increase (as expected) showing that peak current is strongly depend upon the ligand concentration. For higher concentration $4.4 \mu\text{mol l}^{-1}$ a slight decrease in the peak current was observed this effect may be due to the competitive adsorption of APDC with the complex form. An optimum APDC concentration of $3.1 \mu\text{mol l}^{-1}$ was selected for farther studies.

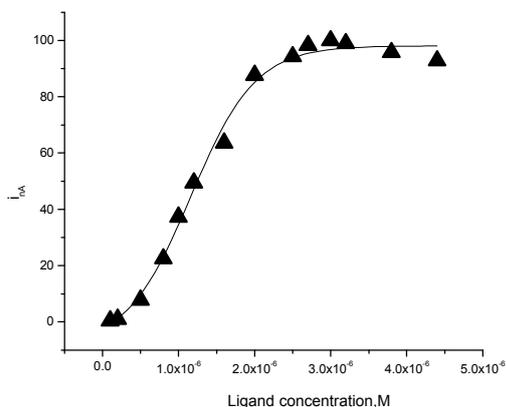


Fig.2: Influence of C_{APDC} on the peak current of the Pb-APDC complex.

Conditions:Pb(II):20ng/ml; pH3.5; E_{acc} :- 0.45V; t_{acc} :60s;scan rate 20mV/s; pulse amplitude :20mV ;and frequency:50Hz.

3.1.3. Effect of accumulation potential:

Fig.3 shows the variation of accumulation potential between -0.6 to -0.1 V with the optimum reagent concentration and other standard measuring conditions remained constant (pH: 3.5; C_{APDC} : $3.1\mu\text{mol l}^{-1}$, t_{acc} : 60s).

The peak current extremely increase from -0.1 to -0.35 v due to increase in the accumulation of Pb-APDC on the surface of the electrode. A decrease in peak current is observed by changing potential from -0.4 to -0.6 v. An accumulation potential of -0.35 V gives the best sensitivity and was chosen for subsequent work. More negative potential values cause electrolysis of Pb(II). Also this decrease in peak current may be due to the adsorption of the ligand on the electrode surface, and thus, cause decrease in the ligand concentration.

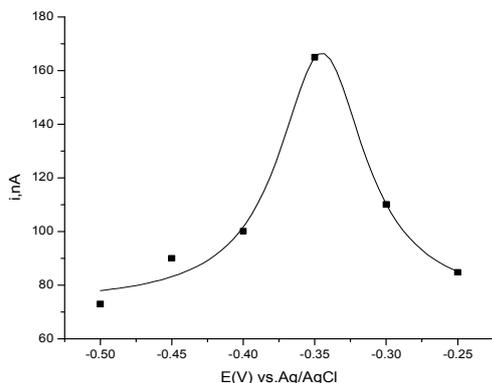


Fig. 3: Influence of E_{acc} on the peak current of the Pb-APDC complex.

Conditions:Pb(II):20ng/ml ; pH 3.5; C_{APDC} $3\mu\text{M}$; t_{acc} :60s; scan rate 20mV/s; pulse amplitude :20mV ;and frequency:50Hz.

3.1.4. Effect accumulation time:

The extent of preconcentration depends on the length of time over which the adsorption is allowed to proceed. The longer the accumulation time, the more pb(II) APDC complex is adsorbed and the larger the peak current observed. The peak current increase almost linearly at first and then curve slightly toward the time axis up to 270 sec, (Fig. 4). Such time dependant profiles represent the corresponding adsorption isotherms, the choice of accumulation time requires a trade-off between sensitivity, speed and selectivity. Thus 180 sec was selected to comprise between sensitivity and speed .Also 180 sec. give sharp peak after this time a broader peak is obtained.

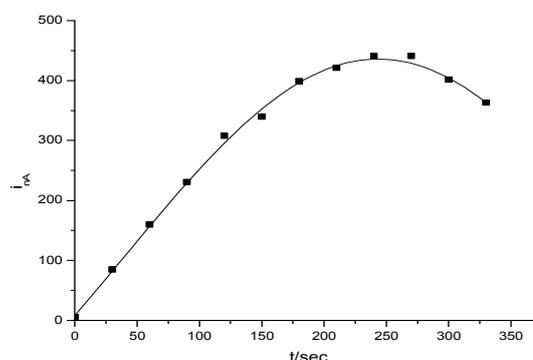


Fig. 4: Influence of t_{acc} on the peak current of the Pb-APDC complex.

Conditions:Pb(II):20ng/ml ; pH 3.5; C_{APDC} $3.1\mu\text{M}$; E_{acc} :- 0.35V; scan rate 20mV/s; pulse amplitude :20mV ;and frequency:50Hz.

3.2 Effect of potential sweep conditions:

3.2.1. Scan rate:

The potential scan rate for SW-AdSV procedure was tested in the range between 2 and 80 mV/sec. and the stripping peak current that was obtained showed a linear dependence on the scan rate (Fig. 5). This linear behavior may suggest that the peak current comes largely from surface adsorbed species [27].

In this work, a potential scan rate 60 mV/sec was chosen and used in all experiments.

3.2.2. Square wave frequency :

The peak current of pb-APDC increased when the frequency increase from 30 to 160 Hz (Fig. 6) and it was concluded that in order to assure maximum peak and more sensitive peak, 150 Hz square - wave frequency was the ideal choice for this operational parameter.

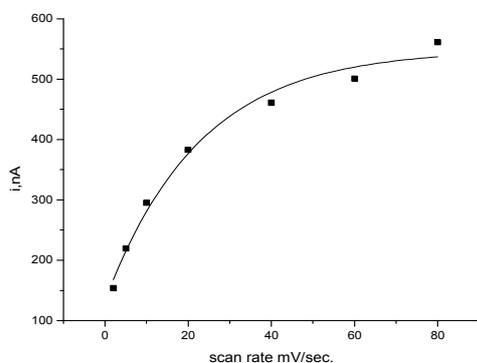


Fig. 5: Influence of scan rate on the peak current of the Pb-APDC complex.

Conditions: Pb(II):20ng/ml ; pH 3.5; C_{APDC} 3.1 μ M; E_{acc} :-0.35V; t_{acc} :180s; pulse amplitude :20mV ;and frequency:50Hz.

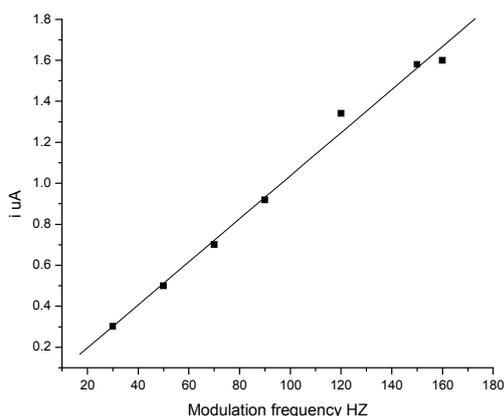


Fig. 6 Influence of frequency on the peak current of the Pb-APDC complex.

Conditions: Pb(II):20ng/ml ; pH 3.5; C_{APDC} 3.1 μ M; E_{acc} :-.35V; t_{acc} :180s; scan rate:60mv/sec ; pulse amplitude :20mV.

3.2.3. pulse amplitude :

Varying the value of excitation wave pulse amplitude (Fig. 7) plays an important role for the measured peak current increasing this parameter over the range 10-50 mV, resulted in extremely enhancement of the voltammetric peak current. As a result 50 mV were adopted as optimum for pulse amplitude.

3.3 Analytical parameters:

Once the most ideal and suitable chemical conditions and instrumental parameters for the stripping voltammetric determination of lead metal

ions were established, calibration plot for this metal ion was recorded to estimate the analytical characteristics of the developed square wave adsorptive stripping voltammetry method.

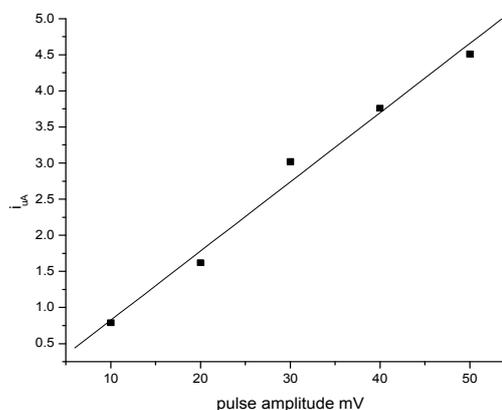


Fig. 7: Influence of pulse amplitude on the peak current of the Pb-APDC complex.

Conditions: Pb(II):20ng/ml ; pH 3.5; C_{APDC} 3.1 μ M; E_{acc} :-0.35V; t_{acc} :180s; scan rate 60mv/sec ; frequency 160Hz.

3.3.1. Calibration graph and detection limit:

The calibration graph (Fig.8) for the determination of lead was obtained under the optimized conditions. The pH : 3.5; C_{APDC} : 3.1 μ mol l^{-1} ; t_{acc} : 180 s ; E_{acc} : -0.35 V. C_{APDC} is 3.1 μ mol l^{-1} , adsorptive curves of pb (II) at concentrations from 5 to 40 ng/ml produce a linear calibration plot ($R=0.99911$) . The precision expressed as the relative standard deviation (RSD) was 0.31535 % for nine successive measurements of the same sample containing 20.0 ng/ml of pb (II). The limit of detection (LOD) is equal to three times the standard deviation of the blank peak current divided by the slope of the calibration curve $3s_b/m$ is equal to 0.89 ng / ml.

3.4 Influence of other metal ions:

To evaluate the selectivity of the method, the influence of many ions on the determination of Pb(II) was examined in the presence of optimum reagent concentration 3.1 μ mol l^{-1} and 20 ng/ml Pb(II). In adsorptive voltammetry interference may arise from competitive adsorption of the ions and their complex or from reduction in the vicinity of the analyte peak the major sources of interference are likely from co-existing metal ions capable of forming complexes with the used chelating agent, hence, affecting SW-AdSV response via an over lapping peak or competing for adsorptive sites on available

ligand. The effect of the following ions, which is of great significance in industrial or environmental matrices, was tested at the optimal experimental conditions. The results of this study on the lead APDC reduction peak are summarized in Table 1.

Table 1: Effect of interfering species on the lead-APDC reduction peak.

Substance added	Concentration (ppb)	Change in i_p %
Zn ²⁺	1000	-4.76
Sr ²⁺	10000	-1.11
Fe ³⁺	3000	-9.31
Ni ²⁺	1000	-13.9
Cd ²⁺	400	-7.06
Cu ²⁺	40	-3.85
Hg ²⁺	100	+2.94
PO ₄ ³⁻	10000	-4.01
HCO ₃ ⁻	10000	-9.29
NO ₃ ⁻	800	-9.25
F ⁻	800	-1.7
Br ⁻	400	-2.8
Cl ⁻	400	-1.1

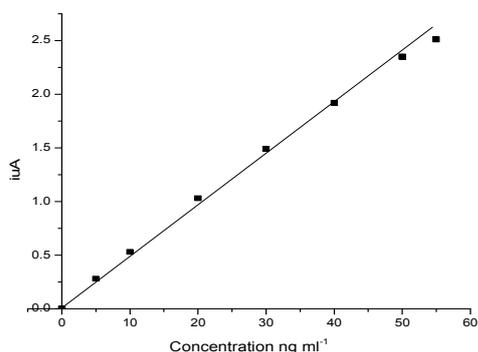


Fig.8: Calibration curve at optimum condition.

3.5 Evidence of complex formation:

Both square wave voltammetry and cyclic voltammetry have been utilized to elucidate and confirm the possible complexation reaction which can occur between lead and ammonium pyrrolidine dithiocarbamate.

Fig. 9 shows an evidence of complex formation between Pb and APDC using square wave voltammograms, this was established as result of tracking the addition of APDC to Pb which produces a series of overlapping signals. Two peaks predominate where one corresponds to a reduction process of free (labile) Pb²⁺ (E_p at -0.36V), this peak current decrease and shifted to more negative potential with the addition of ligand. This behavior may be attributed to the fact that Pb atom is restricted

by two moles 1:2 stoichiometry of the ligand [28-29], so energy is required to reduce such restriction in the complex formed. On the other hand, a new peak is formed (at more positive potential) and its height increase with the addition of the ligand, this peak is related to the reduction

Fig. 10 shows cyclic voltammograms as an evidence of complex formation between Pb and APDC in 0.1 M acetate buffer solution of pH 3.5. As seen from Fig. 10-a, there is an oxidation and reduction peak for APDC at -0.53V and -0.34V which disappear upon the addition of the metal. Pb²⁺ shows reduction and oxidation peaks (Fig.10-c) at -0.40 and -0.35V, respectively which decrease by adding the ligand. A new peak appears at -0.134 and -0.146 V at the same conditions (Fig.10-b) where the Pb-APDC complex formed as a new species.

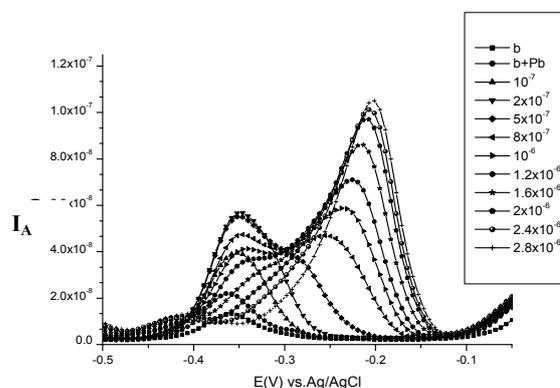


Fig.9: Square wave voltammogram of 20ng ml⁻¹ Pb (II) with different concentrations of APDC

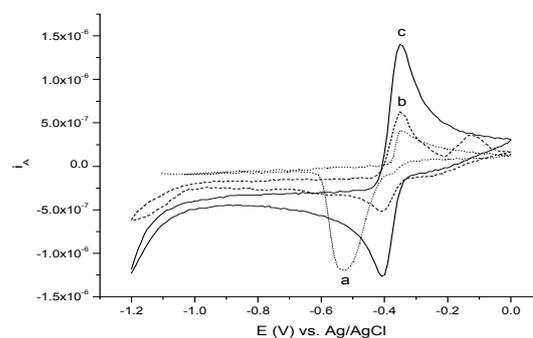


Fig. 10: Cyclic voltammograms of a: 5x10⁻⁴ mol l⁻¹ APDC ,b: 5x10⁻⁴ mol l⁻¹ APDC + 30mg l⁻¹ Pb(II), c: 30mg l⁻¹ Pb(II). pH 3.5,scan rate 500mVsec.⁻¹

3.6 Application:

The utility of the developed method was tested by determining lead in some synthetic mixtures (Table 2) which give good recoveries. The proposed procedure was successfully applied for the determination of the concentration of lead metal in tap water sample by SWASV technique. The sensitivity was calibrated by standard additions to the sample and the initial metal concentrations were calculated by extrapolation. Consequently, linear calibration range was automatically obtained as being related to quantitative mode of the voltammetric unit. As can be seen from Fig.11, the current of the oxidation peak of lead increased by the addition of the standard solution. The concentration of Pb (II) in tap water of Mansoura city (Egypt) was found to be 25 ng ml⁻¹. This value is in the limit values according to TSA, WHO, EPA [30,31].

Table 2 : Determination of Pb(II) 20 ng ml⁻¹ in some synthetic mixtures.

Mixture number	Synthetic mixtures	Recovery
Mixture (1)	NO ₃ ⁻ , PO ₄ ³⁻ , Cl ⁻ , HCO ₃ ⁻ , CO ₃ ²⁻ , F ⁻ , Br ⁻	99%
Mixture (2)	Zn ²⁺ , Fe ³⁺ , Sr ²⁺ , Ni ²⁺	106%
Mixture (3)	Fe ³⁺ , Sr ²⁺ , PO ₄ ³⁻ , Ca ²⁺ , Mg ²⁺ , CO ₃ ²⁻ , HCO ₃ ⁻	94%

(1) anions concentrations 500 ppb
(2) cations concentrations 1000 ppb

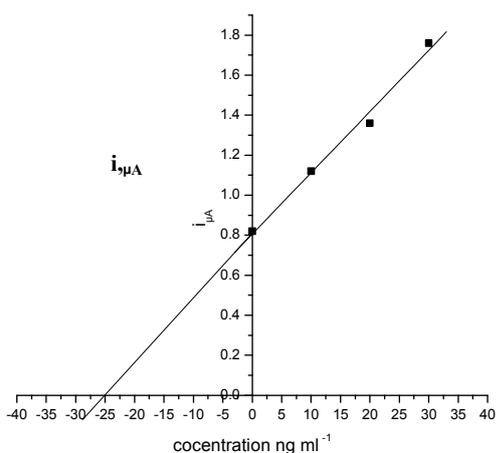


Fig. 11: The calibration plot of Pb(II) obtained from standard addition to tap water sample by SWASV

technique.

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