

A new and simple procedure for the trace determination of mercury using differential pulse polarography and application to a salt lake sample

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Abstract: A new and simple differential pulse polarographic procedure was established for the trace determination of mercury(II). An indirect method had to be used since no polarographic peak can be observed for its direct determination. According to their standard potentials, the reaction between SO_3^{2-} and Hg(II) was suitable. The peak height of sulfite at about -0.70 V (pH 6, 7) was sharp, high, and very reproducible, enabling the accurate determination of low concentrations of Hg(II). It was found that sulfite concentration had to be 3 times larger than mercury at pH 6, in order to have a quantitative reaction.

The procedure is simple: to a known amount of sulfite in the polarographic cell (HAc, pH 6 or 7) is added an unknown Hg(II) sample. The Hg(II) concentration is calculated simply from the decrease in the sulfite peak after reaction with Hg(II). The limit of detection was 1×10^{-6} M (S/N = 3) in this medium, which could not be obtained with most other mercury determination methods. The proposed new method exhibits high selectivity, sensitivity, reproducibility, and accuracy. It was successfully applied to synthetic samples and to a raw salt sample taken from a salt lake (closed basin) in Turkey. No considerable interference was observed from most common ions.

Key words: Differential pulse polarography, mercury in raw salt, salt lake, trace determination

1. Introduction

Trace determination of mercury is important because of its toxic effect on human health. It may be present in many materials as organic or inorganic mercury compounds. It is known as a very complex metal because of its chemical forms and great number of physical states in the environment. Its toxicity and bioavailability depend on its chemical form. Elementary mercury and insoluble HgS are the least toxic. Hg organic compounds, such as methyl mercury (a highly toxic form), may be accumulated in aquatic systems and can enter the food chain.^{1–3} On the other hand, inorganic mercury species are less toxic than the organic compounds. It is known that some soluble mercury compounds can cause serious damage to living organisms and may be deposited in organs.^{4–6}

For the determination of mercury, mostly neutron activation analysis (NAA),⁷ inductively coupled plasma mass spectrometer (ICP-MS),^{8,9} inductively coupled plasma optical emission spectrometer (ICP-OES),¹⁰ cold vapor atomic absorption spectrometer (CVAAS),^{11,12} atomic fluorescence spectrometer (AFS),¹³ and atomic absorption spectrometer (AAS)¹⁴ are used.

The above-mentioned spectroscopic methods can be used safely in the determination of metals in complex matrices; however, they are very expensive when compared with electrochemical techniques. They also need

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preconcentration and extraction, which are time consuming procedures, with danger of losses and contamination. Due to this, the electrochemical techniques emerge with the purpose of eliminating the disadvantages of these high-cost techniques. Their main advantages are high sensitivity, high reproducibility, high selectivity, simple sample preparation, trace metal determination, and direct determination of speciation.

For this purpose, mostly voltammetric methods and modified ion selective electrodes are used. An electrochemical sensor for mercury ions using chelating ionophore was prepared; this electrode could be used in the 5×10^{-6} – 1×10^{-1} M range.¹⁵ For the determination of electropositive elements, a graphite thick film electrode modified with Au(III) was prepared and mercury and arsenic could be determined.¹⁶ In an electrochemical method using anodic stripping voltammetry with a chitosan modified carbon paste electrode mercury determination in water was achieved.¹⁷ Stripping voltammetry using screen printed electrodes has been applied to the determination of mercury and lead traces in tap water.¹⁸ Mercury was determined in ambient air samples¹⁹ and in water samples²⁰ by anodic stripping voltammetry on screen printed gold electrodes. Mercury determination in coal was conducted using an iodide ion selective electrode after elimination of the interference of iron.²¹ With our newly prepared mercury selective electrode, mercury in coal was determined.²² Mercury in table salt was determined by online medium exchange anodic stripping voltammetry.²³ The interference of high chloride content in the determination of mercury was eliminated by reducing its concentration to 3×10^{-3} M. In our DP polarographic method, trace mercury could be determined using the reaction between Sn(II) and Hg(II).²⁴

In our newly established DP polarographic method, mercury can be determined indirectly with a simple and fast procedure. There is no need for any separation or preconcentration, which are time consuming and with danger of contamination. The results obtained with DPP are very reproducible since with the use of a dropping mercury electrode (DME) the behavior of the electrode is independent of its history. No work has been found using polarography, most probably because no polarographic peak is observed for mercury. Thus, it can only be determined indirectly.

2. Results and discussion

Polarography cannot be used directly for the trace determination of Hg(II), since it is not possible to observe it from the polarogram. Thus, an indirect method had to be used. For this purpose, a substance that will react quantitatively with mercury, which is electroactive and which has a sharp and high polarographic peak, had to be chosen. The reduction potentials of Hg(II) and sulfite are +0.86 V and +0.17 V, respectively. According to these potentials, there is a high probability that the reaction between mercury and sulfite will take place quantitatively. While Hg(II) will be reduced into elemental mercury or Hg(I), sulfite ion will be oxidized into sulfate ion. First the reaction conditions, electrolytes, and pH in which this reaction will take place quantitatively have to be determined. For the trace determination of Hg, the peak height of sulfite is also very important, since the decrease in its peak height after the addition of mercury will be measured. No doubt, the larger this change, the more accurate will be the calculation of the concentration of mercury. For this purpose, first the peaks of sulfite were studied in various electrolyte and pH conditions.

2.1. Electrochemical behavior of sulfite

The DP polarograms of sulfite were recorded in various electrolytes such as HCl, HNO₃, and HAc under various pH conditions. It was found that sulfite peaks were sharp and high in the 4–7 pH range (HAc buffer) (Figure 1) and sulfite was stable within this range. There was no decrease in sulfite peak height with time.

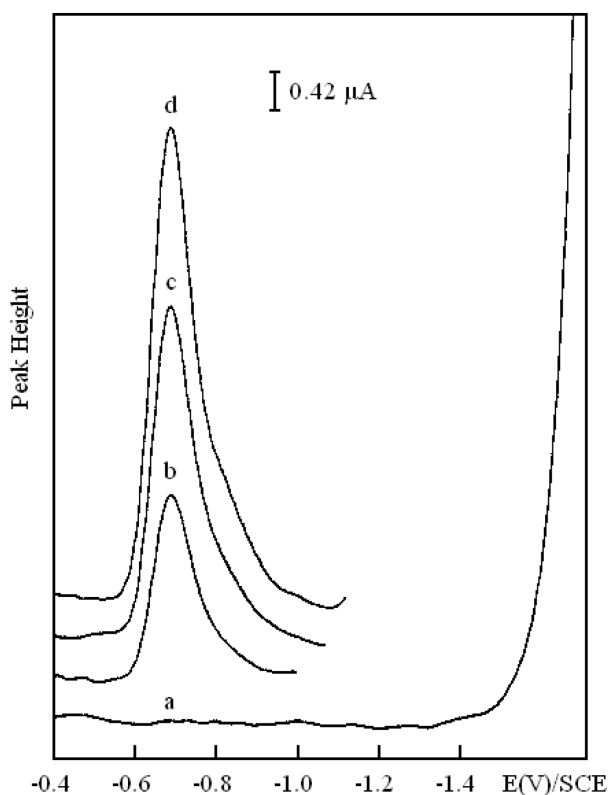
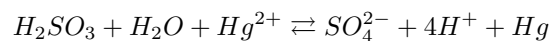


Figure 1. Polarograms of sulfite in HAc (pH 6) medium, a) 10 mL of 0.2 M HAc/Ac- a + 0.1 mL of 1×10^{-2} M SO_3^{2-} , b) b + 0.1 mL of 1×10^{-2} M SO_3^{2-} , c) c + 0.1 mL of 1×10^{-2} M SO_3^{2-} .

In acidic medium at pH values lower than 4, sulfite was unstable because of the formation of SO_2 . As a result, in this medium there will be decay in sulfite concentration with time and the calculation for mercury determination will not be correct. On the other hand, at pH values higher than 7, no sulfite peak was observed.

2.2. Reaction between sulfite and Hg(II)

It is important to find out the optimum reaction conditions in which the reaction is quantitative. For this purpose, the reaction mechanism was followed both at different pH values and at various $\text{SO}_3^{2-}/\text{Hg(II)}$ mole ratios. It was found that this reaction was quantitative in the pH range of 4–6. However, the reaction stoichiometry depended on pH; it was found that two moles of mercury used one sulfite at pH values 4 and 5, that is Hg(II) is reduced into Hg(I). At pH 6, on the other hand, one mercury used one sulfite: Hg(II) is reduced into elemental mercury (Figure 2). This reaction (at pH 6) is preferred, because of the higher decrease in sulfite peak by the addition of unknown mercury. The reaction mechanism at pH 6 can be given as follows:



Since the reaction may be affected also by the $\text{SO}_3^{2-}/\text{Hg(II)}$ mole ratios, the effect of this ratio was also investigated at pH 5 and 6. In a solution containing 3×10^{-5} M Hg (II), at pH 5 when the ratios were taken as 3.3, 2.0, and 1.7, as expected two mercury used one sulfite, but when the ratio was 1.1, no correct determination was possible.

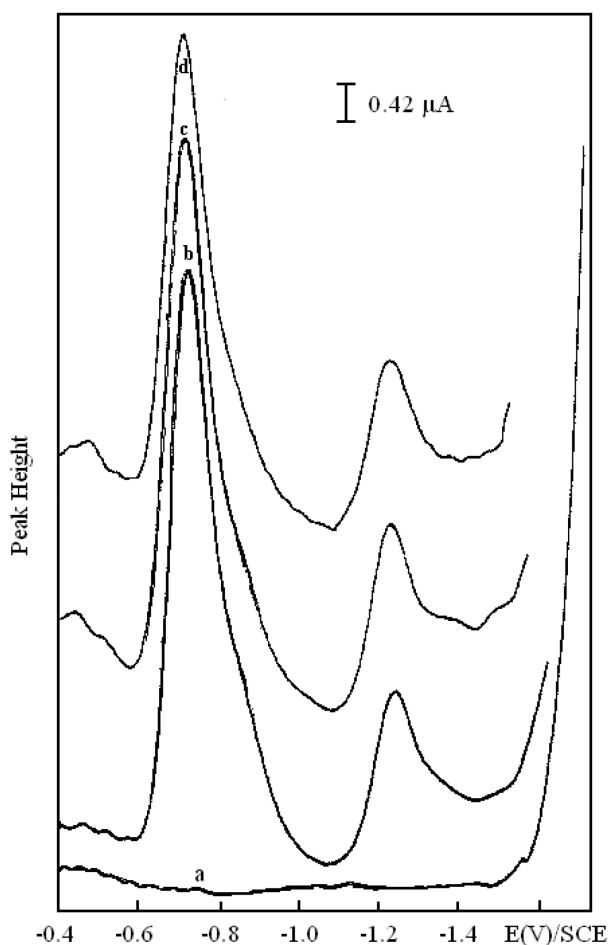


Figure 2. Reaction between sulfite and Hg(II) at pH 6, a) 10 mL of 0.2 M HAc/Ac⁻, b) a + 0.1 mL of 3×10^{-2} M SO₃²⁻, c) b + 0.3 mL of 1×10^{-3} M Hg²⁺, d) c + 0.3 mL of 1×10^{-3} M Hg²⁺.

At pH 6 when the ratios were taken as 10.0, 7.0, 6.6, 6.5, and 2.8 in all these ratios one mercury used one sulfite, but as expected when the ratio was 2.0 or less, again it was not possible to obtain correct results. All these results are summarized in the Table. It can be concluded that the mole ratio of SO₃²⁻/Hg(II) must be larger than 3 at pH 6 (HAc) for safe and reliable measurement. The quantification limit was 2.7×10^{-6} and the LOD of this reaction was 1×10^{-6} M under these conditions, for signal/noise = 3 (S/N = 3).

2.3. Interference studies

The most common cations such as Fe(III), Pb(II), Cd(II), Cu(II), and Zn(II), and anions such as chloride, nitrate, and sulfate were investigated for their interference effect. Cations were studied in two respects of their interference. The first one is because of overlapping peaks with sulfite and the second because of their reduction potentials in order to see the possibility to react with sulfite. These are discussed in two sections as given below.

2.3.1. Interference because of overlapping peaks

In order to see whether there might be any interference because of overlapping peaks, the peak potentials were determined by taking polarograms in HAc, pH 6 reaction medium. The peaks for Fe(III), Pb(II), Cd(II), Cu(II),

and Zn(II) were -0.0 V, -0.40 V, -0.62 V, -0.12 V, and -0.98 V, respectively. Sulfite, on the other hand, had a peak at -0.72 V. As expected, there will be no peak overlap with most of the ions except with Cd(II).

Table. Effect of sulfite/Hg(II) mole ratios (pH 5 and 6) on the reaction stoichiometry.

pH	SO_3^{2-}/Hg^{2+} mole ratio in polarographic cell	Sulfite quantity used by mercury $Hg^{2+}:SO_3^{2-}$ (mole)
5	3.3	3:1.4
	1.7	2.1:1
	2.0	2.1:1
	1.0	Error *
6	10	3:3.1
	7.0	5:5.2
	6.6	3:2.9
	6.0	5:5.2
	5.0	3:3.1
	2.8	3:2.9
	2.2	Error*

*No correct determination

Since the sulfite peak was at about -0.72 V in this medium and the Cd(II) peak was at -0.62 V, a peak overlap is expected only at high concentrations of Cd(II). It was found that sulfite concentration had to be 10 times larger than that of Cd, in order for no peak overlap to exist (Figure 3). This will not create a problem since sulfite concentration has to be at least more than 3 times that of mercury.

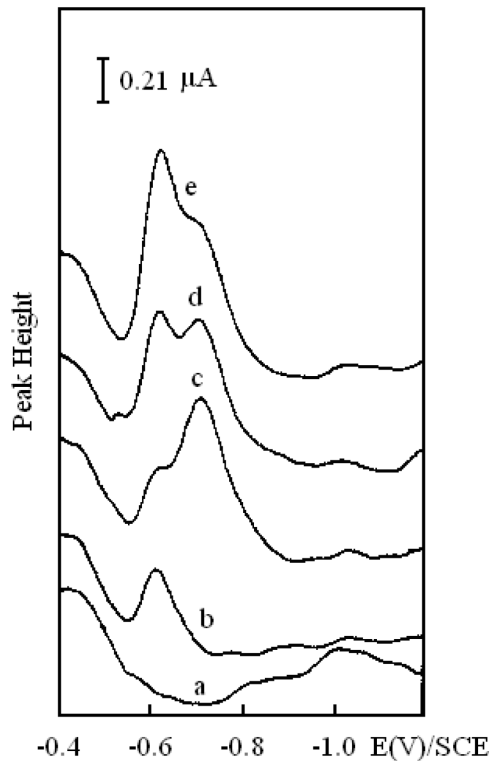


Figure 3. Effect of Cd(II) on sulfite peak at pH 6, a) 10 mL of 0.2 M HAc/Ac-, b) a + 0.1 mL of 1×10^{-4} M Cd^{2+} , c) b + 0.1 mL of 5×10^{-3} M SO_3^{2-} , d) c + 0.1 mL of 1×10^{-4} M Cd^{2+} , e) d + 0.1 mL of 1×10^{-4} M Cd^{2+} .

2.3.2. Interference because of possible reactions with sulfite

Interference because of possible reactions with sulfite was also studied. The standard reduction potentials are important because of the possible redox reactions with sulfite ion. The standard reduction potentials are +0.70 V for Fe(III), +0.34 V for Cu(II), -0.403 V for Cd(II), -0.12 V for Pb(II), -0.76 V for Zn(II), and +0.17 V for sulfate ion. According to these potentials, there is a possibility of a redox reaction between sulfite and Fe(III) (+0.70 V) and Cu(II) (+0.34 V). It was found that there was no decrease in sulfite peak when 2×10^{-5} M Fe(III) was added to 1×10^{-4} M sulfite. However, it started to decrease when Fe(III) concentration was larger. At higher concentrations of Fe(III), this reaction could be eliminated by the addition of fluoride, by complexing Fe(III). In the presence of Cu(II), when to 2×10^{-4} M sulfite was added 1×10^{-4} M Cu no decrease in peak was observed.

2.3.3. Effect of chloride ion

Table salts are known to contain mercury at ultratrace level, as well as a high quantity of chloride ions. In most determination methods it is known that chloride ion shows strong interference not only for mercury ion but for many other ions also. For this reason, chloride ion additions were made to a polarographic cell containing 0.2 M HAc (pH 6) and 2×10^{-4} M sulfite. It was shown that even in the presence of 2×10^{-2} M chloride ion, no effect was observed by the determination of Hg(II) ion.

2.4. Application to a synthetic sample

A synthetic sample containing Fe(III), Cu(II), Pb(II), Zn(II), and Hg(II) each in 2×10^{-3} M concentration was prepared. From this sample an aliquot of 0.1 mL was added to a polarographic cell containing 2×10^{-4} M sulfite in 10 mL of HAc (pH 6) and a polarogram was taken (Figure 4). (Here we have to mention that all ions in polarographic cell are in 1×10^{-5} M). From the decrease in the sulfite peak the mercury content could be determined. To verify the result, standard Hg(II) additions were made and once more mercury quantity was calculated. The result was found for 2×10^{-5} M mercury in the polarographic cell as $(2.1 \pm 0.2) \times 10^{-5}$ M for $N = 5$ and 90% confidence interval.

2.5. Determination of mercury in a raw salt sample taken from a salt lake

The developed method was applied to a raw salt sample taken from a salt lake that is a closed basin. This lake is used for the production of edible salt in Turkey. As experimentally shown in the previous section, there was no effect of chloride on the sulfite peak. About 3 g of dried salt was dissolved in 10 mL of oxygen-free water. A sample of 0.5 mL was taken and added to the polarographic cell containing 0.2 M HAc (pH 6) and 1×10^{-4} M sulfite, a polarogram was taken, and then once more 0.5 mL of sample solution was added in order to see a similar response. The quantity of mercury was determined from the decrease in the sulfite peak. For validation, standard 1×10^{-3} M Hg(II) additions were made as was done in all the above-given cases. The result for Hg(II) in raw salt was $96 \pm 10 \mu\text{g/g}$ Hg(II), for 90% CI and $N = 3$. In our previous work,²⁴ in which we used Sn(II) for reduction, the result found was $102 \pm 9.8 \mu\text{g/g}$ Hg(II), for 90% CI and $N = 3$ for the salt sample taken from the same lake.

The proposed procedure is quite simple: to a known amount of sulfite in the polarographic cell (HAc, pH 6-7), an unknown Hg(II) sample is added. The Hg(II) concentration is calculated simply from the decrease in the sulfite peak after reaction with Hg(II). The limit of detection (LOD) was 1×10^{-6} M ($S/N = 3$) in this

medium, which could not be obtained with most other mercury determination methods. Only in our previous DP polarographic method,²⁴ in which we used Sn(II) for the reduction of Hg(II), the LOD was 4×10^{-7} M, which is lower than that of our newly established method, in which we used sulfite. However, while the sulfite solution can be stored for at least 1 week, the preparation and protection of Sn(II) is not so easy (it has to be prepared every day). Here it has to be mentioned that when Sn(II) was used, the pH had to be about pH 6, and for sulfite it had to be about pH 2. Thus, according to the sample medium the pH and also the reducing agent can be chosen.

No considerable interference was observed from most common ions. Fe(III) at higher concentrations will react with sulfite present, but this reaction could be eliminated simply by the addition of fluoride by complexing Fe(III). The proposed method can be applied safely to many biological samples.

3. Experimental

3.1. Apparatus

A polarographic analyzer, ENTEK Electronics Model 2016, equipped with a mercury drop timer was used. The drop time of the electrode was in the range 2–3 s (2.4 mg s^{-1}). A Kalousek electrolytic cell with a saturated

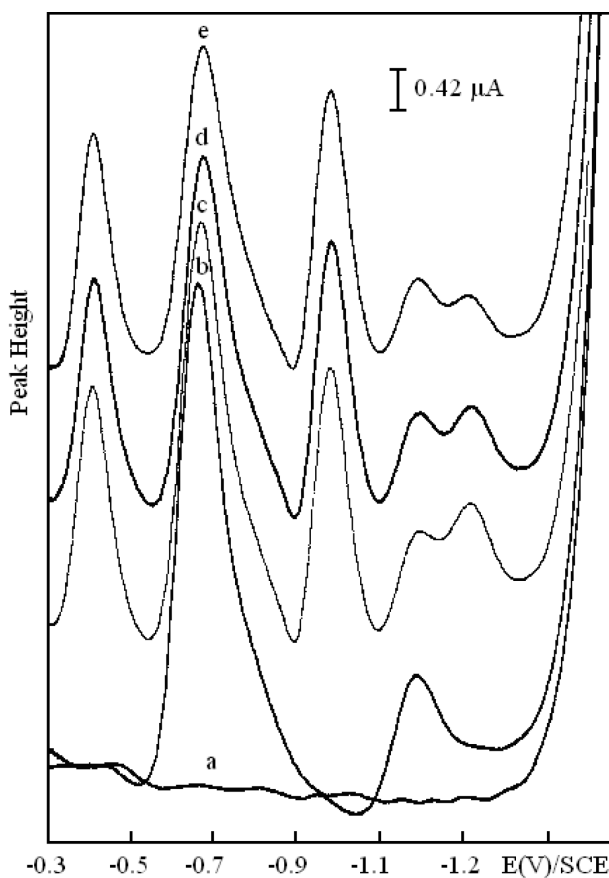


Figure 4. Determination of Hg(II) in a synthetic sample (pH 6), a) 10 mL of 0.2 M HAc/Ac⁻ b) a + 0.1 mL of 2×10^{-2} M SO₃²⁻, c) b + 0.1 mL of sample, d) c + 0.1 mL of 2×10^{-3} M Hg²⁺, e) d + 0.1 mL of 2×10^{-3} M Hg²⁺, Sample: Fe(III), Cu(II), Zn(II), and Hg(II) each in 2×10^{-3} M.

calomel electrode (SCE), separated by a liquid junction, was used in the three-electrode configuration. The counter electrode was platinum wire. The polarograms were recorded with a Linseis (LY 1600) X-Y recorder under the conditions of a drop life of 1 s, a scan rate of 2–5 mV s⁻¹, and pulse amplitude of 50 mV.

3.2. Reagents

All chemicals used were of analytical-reagent grade (proanalysis). Triply distilled water was used in the preparation of all solutions. Solutions of 1×10^{-3} M and more dilute ones were prepared before every use in order to avoid the aging process of solution. In order to expel the oxygen present in the polarographic cell 99.999% pure nitrogen was passed through the solution.

The mercury (proanalysis) used in the dropping mercury electrode was obtained from Merck (Darmstadt, Germany). Contaminated mercury was cleaned by passing it successively through dilute HNO₃ (3.0 M) and water columns in the form of fine droplets by using a platinum sieve. This mercury was then washed in the same way until no acidic reaction was observed. The collected mercury was stored in a closed vessel covered with water. It was dried between sheets of filter paper when it was needed. The mercury used was not lost since it was collected quantitatively, without causing any pollution. Thus, no mercury loss is possible and it can be used continuously. Before use, a DPP polarogram of this mercury was recorded each time in order to confirm the absence of impurities.

3.3. Preparation of reagents

1.0 M HAc/Ac⁻ buffer: It was prepared by adding 6 g of solid NaOH to 57 mL of 1.0 mol L⁻¹ HAc; after it was washed with distilled water in order to remove the carbonate formed and diluted to 1 L. The pH was adjusted to the desired value using a pH-meter.

0.1 M Hg(II) solution: To 3.43 g of Hg(NO₃)₂.H₂O were added 30 mL of distilled water and 1.0 mL of HNO₃, followed by dilution with distilled water to 100 mL using a volumetric flask.

0.2 M Sulfite solution: 0.252 g of Na₂SO₃ was dissolved in 10 mL of aerated distilled water. It was kept with Zn granules in order to prevent air oxidation. This solution was prepared each week newly.

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