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DIFFERENTIAL PULSE POLAROGRAPHIC DETERMINATION OF ARSENIC IN BITUMINOUS COAL

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ABSTRACT. *Differential pulse polarography was employed for the determination of arsenic in bituminous coal from Figueiras, Parana, Brazil. The dried coal sample was crushed to ~ 100 mesh, ashed and treated with reducing reagents in acidic media. The arsine generated was collected and selectively oxidized to* As^{3+} *using an absorbing solution of* $0.1\ mol.L^{-1}$ *[tris(hydroximethyl) aminomethane] (TRIS) and* $0.002\ mol.L^{-1}$ *silver nitrate. A solution of TRIS and hydrochloric acid, pH ~ 1, was used as supporting electrolyte for differential pulse polarographic determination of* As^{3+} *in the concentration range 0.05 - 0.60 μg/mL. The average arsenic concentration found was* $69.0 \pm 2.6\ mg.kg^{-1}$ *and was in agreement with the spectrophotometric method using silver-diethyldithiocarbamate-pyridine.*

RESUMO. *O teor de arsênio em carvão betuminoso de Figueiras, Estado do Paraná, Brasil, foi determinado por polarografia de pulso diferencial. Após a secagem o carvão foi triturado a ~ 100 mesh, calcinado e, a seguir, tratado com agentes redutores em meio ácido. A arsina foi coletada e seletivamente oxidada a* As^{3+} *utilizando como solução absorvedora o TRIS [tris(hidroximetil)aminometano]* $0,1\ mol.L^{-1}$ *e nitrato de prata* $0,002\ mol.L^{-1}$*. Uma solução de TRIS e ácido clorídrico, pH ~1, foi utilizada como eletrólito suporte na determinação de* As^{3+} *por polarografia de pulso diferencial, no intervalo de concentrações de 0,05 a 0,60* $\mu g.mL^{-1}$*. A concentração média do arsênio encontrado foi de* $69,0 \pm 2,6\ mg.kg^{-1}$ *concordando com o método clássico espectrofotométrico de dietilditiocarbamato de prata e piridina.*

Key words: arsenic, bituminous coal, differential pulse polarography, spectrophotometry.

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INTRODUCTION

Arsenic is a constituent of numerous minerals and is found most frequently in association with sulfur, especially as arsenopyrite, palladium as arsenopalladinite, gold, uranium, etc [1]. Soils associated with gold deposits contain between 300 and 5000 p.p.m. of arsenic compounds. This association of arsenic with valuable elements has led to suggestion of its use as a geological prospecting marker. The arsenic content of plants could be used as a biogeochemical indicator, in particular, as a pathfinder element for gold [2].

Arsenic is also present in coal, shale oil, and petroleum. The redistribution of arsenic by fossil combustion has important environmental consequences. Natural phenomena such as wheathering, antropogenic imputs, biological and volcanic activity are responsible for the emission of arsenic into the atmosphere [3,4].

Coal produces up to 30 % of its weight as fly ash after combustion, and increased coal usage presents problems regarding the disposal of this material[5]. Arsenic concentrations in groundwater are usually below 5 μg.L^{-1} , but geochemical mobilization, contaminated soils in industrial regions and the use of arsenic pesticides lead locally to enhanced concentrations [6,7,8]. In natural waters the speciation and distribution of dissolved arsenic are influenced by the differential scavenging of As(III) and As(V) by iron and manganese oxides[9,10]. Generally, adsorption of arsenite is relatively lower as compared to arsenate ions[7].This paper presents a novel procedure for arsine generation and determination of As(III) in bituminous coal by means of differential pulse polarography(DPP).

EXPERIMENTAL

Apparatus

A polarograph (Radelkis-Hungary-OH-107), with a platinum wire in contact with mercury pool as reference electrode, scan rate (2 mV.sec^{-1}) , pulse amplitude (50 mV.sec^{-1}), sensitivity of 0.2 μA, and mercury dropping time of 2 sec were employed. Spectrophotometric determination of As:DDTC: pyridinium complex[11] was performed with UV-VIS spectrophotometer Beckman DU-70 and 1 cm quartz cubets.

Reagents

Nitric acid (d = 1.40, Merck); hydrochloric acid, 37%, Merck; tris(hydroxymethyl)aminomethane, 99 % - TRIS, Sigma, and standard reference of bituminous coal (3.72 mg.kg^{-1}), National Institute of Standards and Technology-USA were used. The following chemicals (Aldrich-USA) were also employed:Thallium(III) nitrate trihydrate,98 %; tellurium(IV) chloride, 99 %; germanium tetrachloride; selenium(I) chloride; antimony(III) oxide, 99%; tin(II) chloride, 98%; Arsenic free granulated zinc ,100 mesh; silver nitrate, 99%; potassium iodide, 99%; arsenic(III) oxide, 99%; diethyldithiocarbamic acid, silver salt, 99%; AgDDTC; pyridine, 99%.

Arsine generation

Coals samples were obtained from the **CNEN** (National Commission of Nuclear Energy - Brazil) site located 3 miles northwest of Figueiras, Paraná, Brazil. Figueiras has one of the most important deposits of bituminous coal in Paraná State, mainly because of its uranium content (see Table 1).Dried coal samples were ground to ~ 100 mesh and 3.00 g were transferred to a porcelain crucible and ignited at 450°C for 3 hours. After cooling, the sample was transferred to a flask A as shown in Figure 1. Five mL of concentrated HCl, 5.0 mL (0.1 mol.L^{-1}) KI, 0.50 mL (1.0 mol.L^{-1}) $SnCl_2$, and 1.50 g of granulated Zn were also added to the same flask[11]. After conecting the flasks A and B, the arsine generated in flask A was absorbed in flask C with a solution of 0.020 M $AgNO_3$ and 0.10 M TRIS, at pH 6.2. The absorbed arsine was then selectively oxidized to As^{3+} in this medium. The glass wool and lead acetate in flask B were used for sulfide hydrogen absorption.

Differential pulse polarographic determination of As^{3+}

An acidic solution, pH ~ 1, of 0.10 mol/L TRIS-HCl was employed as supporting electrolyte for DPP measurements at the dropping mercury electrode. An aliquot of 1.00 mL of standard solution of As^{3+} prepared from As_2O_3 was added to the polarographic cell containing 2 mL of pure mercury, and 10.0 mL of supporting electrolyte. Deaeration was performed with pure nitrogen for 15 minutes and the polarograms recorded from 0 to - 1.6 volts. The optimum concentration range observed in the polarographic cell was 0.05 - 0.60 μg(As).mL^{-1} as measured from standard curves.

Two different methods of standard addition were used for arsenic determination in bituminous coal. 1) Addition of known concentration of As^{3+} to the flask used for arsine generation, recording the polarogram after addition of the sample (1.00 mL) to the polarographic cell with a known concentration of As^{3+}. This polarogram was compared with the polarogram of the sample added to the polarographic cell, without addition of standard solution of As^{3+} for arsine generation. 2) A polarogram with a known concentration of As^{3+} was recorded. A new polarogram was recorded again after addition of the sample (1.00 mL) to the polarographic cell. Standard reference of bituminous coal (3.72 mg (As).kg^{-1}) was used to compare the efficiency of the proposed method.

The classical spectrophotometric method of Gutzeit measuring the color formed by the reaction of arsine and a solution of silver diethyldithiocarbamate (AgDDTC)-pyridine was also used for comparative purposes[11]. Interference studies of substances that also form volatile hydrides were performed after addition of 10μg.ml^{-1} of each solution to flask (A) before arsine generation.

RESULTS AND DISCUSSION

As^{3+} recorded from acidic media undergoes three distinct reduction steps(Figure 2). The only important peak for quantitative purposes is E_p = -0.45 volts where the reaction is diffusion-controlled and proportional to the As^{3+} concentration in the polarographic cell.

The following reactions probably occur in flasks A (arsine generation[11]), B(selective oxidation to As^{3+}), and the polarographic cell respectively:

$$As_2O_5(s) + 10\,H^+ + 4\,e \Rightarrow 2\,As^{3+} + 5\,H_2O$$
$$As^{3+} + 3\,Zn(s) + 6\,HCl(aq.) \Rightarrow AsH_3(g) + 3\,ZnCl_2 + 3\,H^+ \qquad (A)$$
$$6\,Ag^+ + AsH_3(g) \Rightarrow As^{3+}(aq.) + 6\,Ag(s) + 3\,H^+ \qquad (B)$$
$$As^{3+}(aq.) + 3\,e = As(s) \qquad E_p = -0.45 \text{ volts} \qquad (\text{polarographic cell})$$

Table 1. Coal Reserves in Parana State[12]

District	coal (tonne - in situ)	% of total
Ortigueira	2,227,000	2.9
Figueiras	31,200,000	40.4
Telemaco Borba	1,800,000	2.3
Sapopema	42,000,000	54.4
Total	77,277,000	100

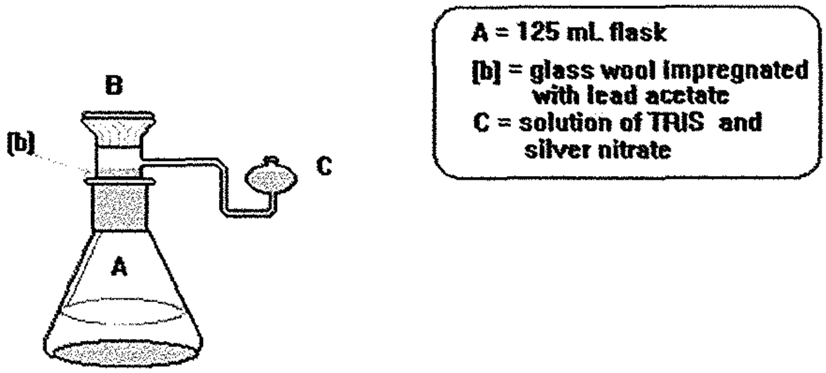

Figure 1. Apparatus used for arsine generation

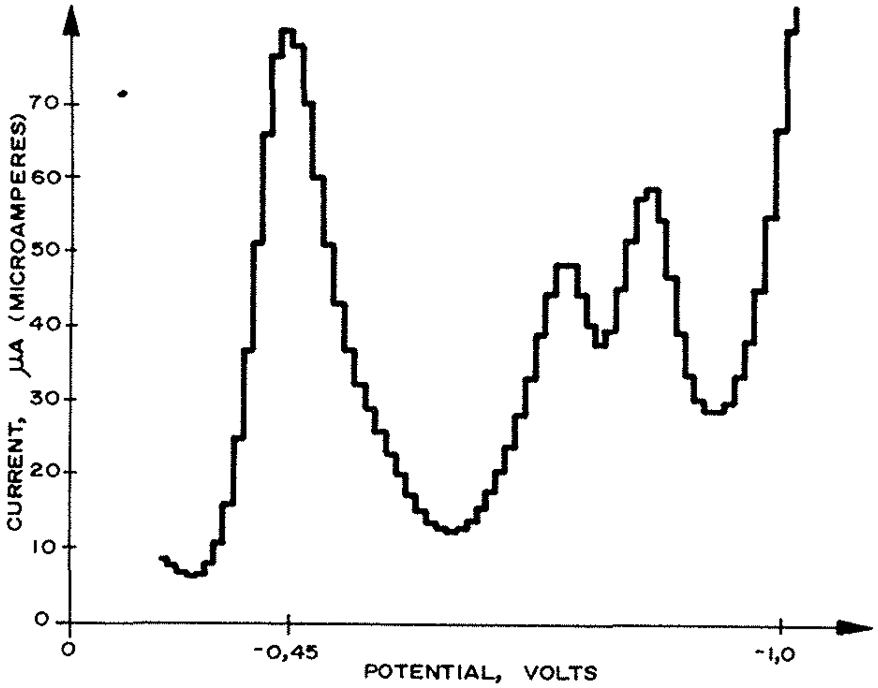

Figure 2. Differential pulse polarography (DPP) of As^{3+} in TRIS-HCL as supporting electrolyte.

Table 2. Arsenic Found in Bituminous Coal from Figueiras, PR., Brazil.

Samples	spectrophotometry ($mg.kg^{-1}$)	DPP ($mg.kg^{-1}$)*
1	68.77	67.26
2	64.78	66.89
3	69.49	73.00
4	65.03	67.81
5	71.04	72.77
6	64.54	69.14
7	69.18	70.16
8	72.24	72.64
Average	68.06 ± 2.99	69.96 ± 2.57

Spectrophotometric conditions: $\lambda = 540$ nm; range of As^{3+} concentration 0.5 - 3.0 μg/mL

(*) Average of 5 determinations.

DPP = Differential Pulse Polarography.

The I_p observed at - 0.45 volts was proportional to As^{3+} concentration. No interferences were observed with tellurium (IV) , thallium (III), germanium(IV), antimony (III) , and selenium(I). Table 1 summarizes some important coal deposits in Parana State, Brazil. Figueiras is the most important reserve because of its uranium content[12] . Table 2 shows the arsenic content found in bituminous coal from Figueiras by DPP (differential pulse polarography) and spectrophotometric methods.

The proposed method of arsenic determination by differential pulse polarography is very simple and useful for a complex samples like bituminous coal. Using the standard addition method for arsine generation, the recovery of As(III) was almost complete and no systematic error was observed. The results were in agreement with the spectrophotometric method using silver diethyldithiocarbamate-pyridine solution.

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