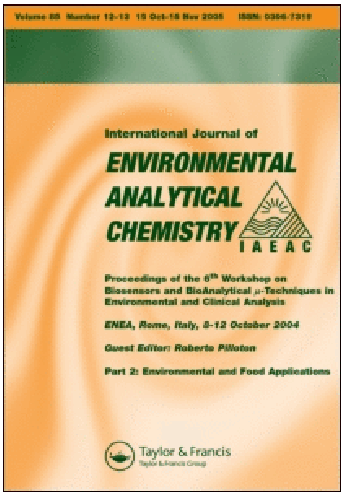

**International Journal of Environmental Analytical Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# Differential Pulse Polarographic Determination of Uranium in Bituminous Coal

E. M. Nogami[a]; G. M. Dálmeida-Oliveira[b]; J. Nozaki[c]
[a] Ecology of Aquatic and Continental Environments-UEM, Maringa, Parana, Brazil [b] Federal University of Amazonas-UFA, Maringa, Parana, Brazil [c] Departamento de Química, Av. Colombo 5790, Universidade Estadual de Maringá, Maringa, Parana, Brazil

**To cite this Article** Nogami, E. M. , Dálmeida-Oliveira, G. M. and Nozaki, J.(1997) 'Differential Pulse Polarographic Determination of Uranium in Bituminous Coal', International Journal of Environmental Analytical Chemistry, 68: 1, 25 — 31

**To link to this Article: DOI:** 10.1080/03067319708030477

**URL:** http://dx.doi.org/10.1080/03067319708030477

*Intern. J. Environ. Anal. Chem.*, Vol. 68, pp. 25-31
Reprints available directly from the publisher
Photocopying permitted by license only

# DIFFERENTIAL PULSE POLAROGRAPHIC DETERMINATION OF URANIUM IN BITUMINOUS COAL

E.M. NOGAMI[a], G. M. DÁLMEIDA-OLIVEIRA[b] and J. NOZAKI[c], *

[a]*Ecology of Aquatic and Continental Environments-UEM;* [b]*Federal University of Amazonas- UFA;* [c]*Departamento de Química, Av. Colombo 5790, Universidade Estadual de Maringá. 87020–900 Maringa, Parana, Brazil*

*(Received 15 November, 1996; In final form 10 February, 1997)*

A liquid-liquid extraction and determination of uranyl ion in coal ash have been investigated. Synergistic effects were observed using a combination of thenoyltrifluoracetone, tributyl phosphate, and methyl isobutyl ketone. After the separation of interfering ions by precipitation with a hot ethanolic solution of thioacetamide, the determination of uranyl ion was performed by differential pulse polarography using a solution of 1.0 M TRIS-HCl as supporting electrolyte. The average uranium content in bituminous coal was in agreement with the spectrophotometric method using 4-(2-pyridylazo)resorcinol.

*Keywords:* Uranium; bituminous coal; synergistic extraction; differential puse polarography

## INTRODUCTION

Bituminous and sub-bituminous coals are largely used in ceramics, steel, cement, chemical, paper, textile, and plastics industries. Uranium and other minerals are concentrated in the ash, when coal is burned, and the recovery of uranium is important for safety and economic reasons. 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[1].

Liquid-liquid extraction techniques for the recovery of uranium and transuranic elements from coal ash and acid waste solutions have been proposed[2]. Sev-

---

* To whom correspondence should be addressed, Fax: +55–44–223 2676. E-mail : jorgenozaki@cybertelecom.com.br.

eral methods are used for uranyl ion extraction, for instance, tributyl phosphate (TBP) diluted in a hydrocarbon solvent, some phosphine oxides such as tri-n-octylphosphine oxide (TOPO), etc[3, 4].

The efficiency has been improved using supercritical fluid extraction (SFE) with carbon dioxide, and the extraction is strongly dependent on nitric acid concentration[5]. Synergistic effects were also observed using TBP and β-diketones in the extraction of lanthanides, uranium and thorium by liquid-liquid extraction and supercritical carbon dioxide[6,7].

Adsorptive stripping voltammetry (ASV) and differential pulse polarography (DPP) are currently used as electroanalytical techniques for uranium quantification after liquid-liquid extraction[8,9,10,11]. Spectrophotometric methods are also employed for the determination of trace levels of uranium in lake water[12], geological samples[13], cassiterite mineral[14], rocks[15], and synthetic mixtures of inorganic ions by high-order derivative spectrophotometry[16].

In this paper, a novel procedure of separation, synergistic extraction of uranyl ion from acidic solution and determination by DPP has been investigated. The spectrophotometric method measuring the pink colour formed by the reaction of uranyl ion and 4-(2-pyridylazo)resorcinol (PAR) was used for comparative purposes.

## EXPERIMENTAL

### Sample preparation

Coals samples were obtained from CNEN (National Commission of Nuclear Energy) located 3 miles northwest of Figueiras, Parana, Brazil. Figueiras has one of the most important coal deposits in Parana State, because of its uranium content (Table I).

The samples were grounded to ~ 100 mesh, and 4.0 g of powder were transferred to a porcelain crucible and ignated at 750 °C. The residue was transferred to a Teflon tube containing 10.0 ml of distilled water and 15.0 ml of a mixture of concentrated HCl and $HNO_3$ (1:1). It was introduced into a stainless steel digestion bomb for 2 hours at 110 °C. After cooling the sample was filtered and the residue of $SiO_2$ was discarded.

TABLE I Coal reservations in Parana State and average concentration of $U_3O_8$ found

| *District* | *coal (tonne- in situ)* | *$U_3O_8$ % (w/w)* |
|---|---|---|
| Ortigueira | 2,227,000 | < DL |
| Figueiras | 31,200,000 | 0.31 |
| Telemaco Borba | 1,800,000 | < DL |
| Sapopema | 42,000,000 | < DL |

DL = detection limit = $5.0 \times 10^{-8}$ M ($U_3O_8$)
< DL = lower than detection limit

## Separation of interfering substances

An ethanolic solution of thioacetamide (TAA), 2% (w/w) (Aldrich), was employed for precipitation and separation of molybdenum, arsenic, lead, cadmium, and mercury as sulfides, at the temperature of ~ 60 °C. After filtering and washing with distilled water, the filtrate containing $UO_2^{2+}$, adjusted to pH 3.5, contaminated with $Fe^{3+}$, $Al^{3+}$, $Ca^{2+}$, $Mg^{2+}$, and traces of Mo(VI), $Cd^{2+}$, and $Pb^{2+}$, was transferred to a separatory funnel. Liquid-liquid extraction were carried out after shaking for 15 minutes with 10.0 ml of a mixture of 20 % (v/v) TBP (Aldrich) in methyl isobutyl ketone MIK (Merck) , 0.5 M thenoyltrifluoracetone (TTA) ( Sigma), repeating the procedure 5 times. From the total volume of organic phase (50 ml), the back-extraction was performed with ammonium acetate 25 % (m/v),(Merck).

## DPP determination of uranyl ion

One milliliter of the aqueous extract was pipetted into the polarographic cell containing 10.0 ml of supporting electrolyte (0.1 M TRIS-HCl), (TRIS) tris(hydroxymethyl)aminomethane and 2.0 ml of pure mercury. After deaeration of the solution with pure nitrogen for 10 minutes, the DPP was started with the following conditions: Polarograph (Radelkis- Hungary-OH–107), reference electrode (platinum wire), scan rate (2 $mV.sec^{-1}$), pulse amplitude (50 $mV.sec^{-1}$), sensibility (0.2 μA), mercury dropping time (t = 2 sec).

The measurements were repeated after addition of standard solution of uranium nitrate (uranyl nitrate hexahydrate, Merck ) in the range of 1 – 5 μg. ( $UO_2^{2+}$ ) $ml^{-1}$ prepared from stock solution (1000 $mg.l^{-1}$ ( $UO_2^{2+}$ )) to the polarographic cell, to quantify the uranium concentration in the sample. A reference sample $S_4$ (International Atomic Energy Agency), a low grade uranium ore (uraninite), with 0.378 % of $U_3O_8$ was used, in the same procedure, to check the precision and accuracy of the proposed method.

### Spectrophotometric determination of uranyl ion

In order to compare the DPP and spectrophotometric methods, the determination of uranyl ion from the aqueous extract was performed by the complexometric reaction with PAR (Merck) using the procedure of Grudpar, et al[14]. The pink colour of the complex ($\lambda = 530$ nm) was measured with the spectrophotometer UV/VIS-GBC-918.

## RESULTS AND DISCUSSION

Trace amounts of molybdenum cadmium, and lead do not interfere with the determination of uranium by DPP as shown in Figure 2. This is important because Mo(VI) in nitric acid or nitrate media shows strong catalytic activity. Only very small amount of uranyl ion is lost by co-precipitation with sulfides of Mo, Cd, Pb, As, and Hg, as shown in Figures 1 and 3. On the other hand, even small amounts of foreign ions interfere with the spectrophotometric method. During the spectrophotometric measurements of the complex uranyl:PAR, solutibns of NaF (5%, m/v, Merck ), EDTA (10 % , m/v, Merck), and triethanolamine (TEA, pH = 8, Merck) were used as masking solutions for Mo(VI). $Pb^{2+}$, $Cd^{2+}$, $Al^{3+}$, and $Fe^{3+}$.

Molybdenum is a main component of foreign ions in bituminous coal and the determination of Mo(VI) by DPP was also investigated. As shown in Figure 1, after acidic digestion of sulfides and pH adjustment (pH = 5.0), Mo(VI) is synergistically extracted by a mixture of ammonium pyrrolidine dithiocarbamate (APDC, 0.10 M, Merck), TTA (0.5 M, Sigma), and $CHCl_3$. Small amounts of $Cd^{2+}$, $Pb^{2+}$, $VO_2{}^+$, and traces of $UO_2^{2+}$ were co-extracted and did not interfere with the differential pulse polarographic determination of molybdenum (Figure 3).

## CONCLUSIONS

The proposed method incorporates the advantages of synergistic extraction, separation, preconcentration, and DPP determination of uranium in a complex sample such as bituminous coal. The results of DPP determination of uranyl ion were in close agreement with the classical spectrophotometric method using PAR as complexing reagent.

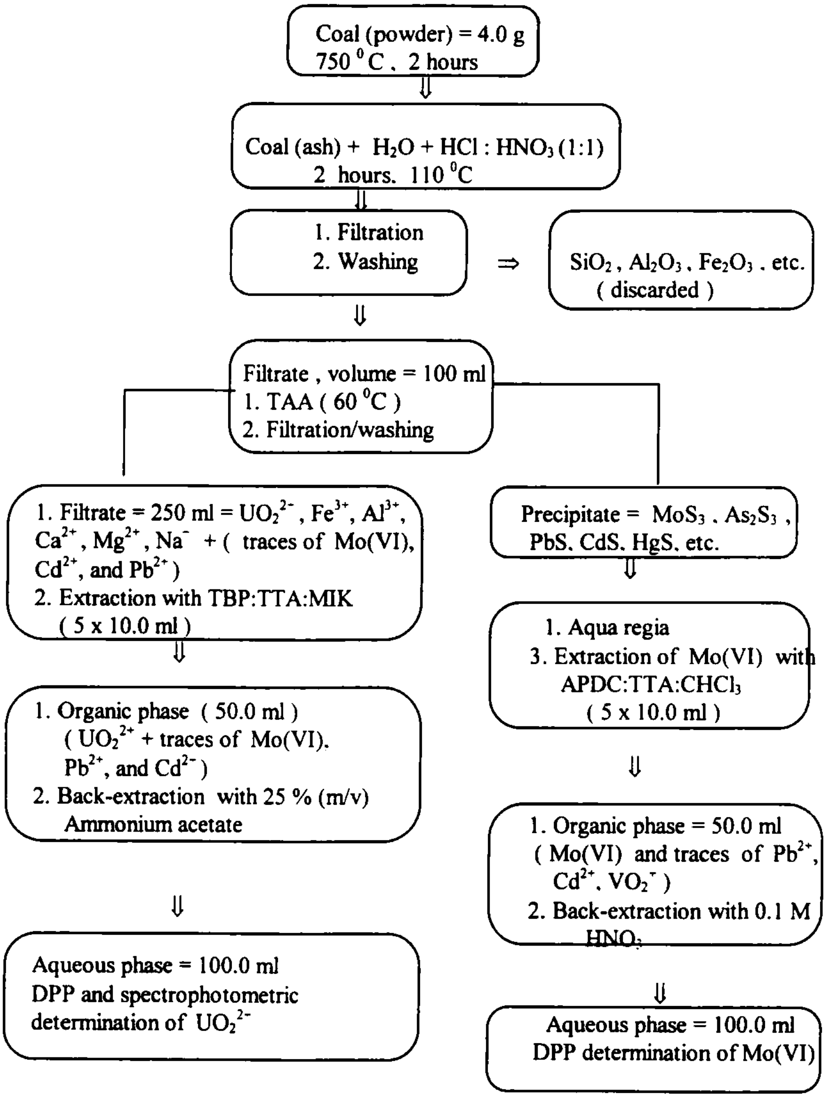

FIGURE 1 Schematic diagram for sample preparation and determination of $UO_2^{2+}$ and Mo(VI)

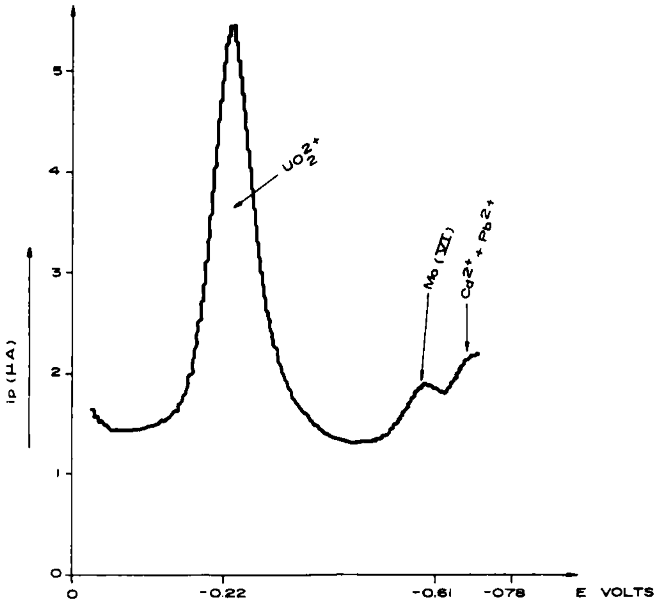

FIGURE 2 Differential puise polarogram of $UO_2^{2+}$ extracted with TBP T TTA/ MIK

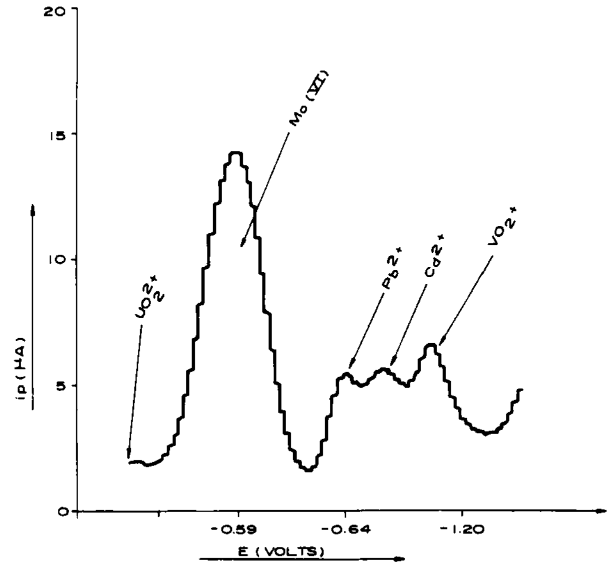

FIGURE 3 Differential pulse polarogram of ions extracted with APDC / TTA / $CHCl_3$

TABLE II Uranium concentration in bituminous coal of Figueiras-PR

| *Sample number* | *spectrophotometry (%, w/w)* | *DPP (%, w/w)* |
|---|---|---|
| 1 | 0.20 | 0.27 |
| 2 | 0.28 | 0.33 |
| 3 | 0.32 | 0.31 |
| 4 | 0.33 | 0.29 |
| 5 | 0.36 | 0.34 |
| Average (*) | 0.30 ± 0.06 | 0.31 ± 0.03 |

(*) Each sample = average of 6 determinations

## *Acknowledgements*

The authors thank CNPq/CAPES/FNMA (Brazil) for financial support. We also thank Dr. Norbert Mikeley (PUC/RJ) and Dr$^a$. Maria Inês Cantagallo-IPEN-CNEN-SP for providing standard samples of uranium mineral ores.

## *References*

[1] D. C. Perricos and E. P. Belkas. *Talanta*, **16,** 745–748 (1969).
[2] V. M. Shinde and N. G. *Bhilare. Analyst*, **120,** 391–393 (1995).
[3] V. K. Manchanda, P. K. Mohapatra and R. Veeraraghavan. *Anal. Chim. Acta*, **320,** 151–154 (1996).
[4] Y. Lin, N. G. Smart and C. M. Wai. *Environ. Sci. Technol.*, **29,** 2706–2708 (1995).
[5] J. T. V. Elteren Van, C. M. G. Van den Berg, H. Zhang, T.D. Martin and E. P. Achterberg. Anal. Chem., **67,** 3903–3910 (1995).
[6] K. E. Laintz and E. Tachikawa. Anal. Chem., **66,** 2190–2193 (1994).
[7] C. M. Wai and Y. Lin. *Anal. Chem.*, **66,** 1971–1975 (1994).
[8] M. A. Ghandour and A. M. M. Ali. *Analyst*, **120,** 1065–1068 (1995).
[9] C. Degueldre and K. Taibi. *Anal. Chim. Acta*, **321,** 201–207 (1996).
[10] R. Djogié and M. Branica. *Analyst*, **120,** 1989–1993 (1995).
[11] M. H. Pournaghi-Azar and R. Zargharian. *Anal. Chim. Acta*, **328,** 33–39 (1996).
[12] Y. Ru, L. Yan, S. Guilan, W. Tao and P. Jiaomai. *Anal. Chim., Acta* **314,** 95–99 (1995).
[13] N. Nashine and R.K. Mishra *Analyst*, **120,** 197–199 (1995).
[14] K. Grudpan, P. Sooksamiti and S. Laiwraungrath. *Anal. Chim. Acta*, **314,** 51–55 (1995).
[15] K. Grudpan, S. Laiwraungrath and P. Sooksamiti. *Analyst*, **120,** 2107–2110 (1995).
[16] N. Agnihotri, V.K. Singh and H.B. Singh. *Analyst*, **120,** 1809- 1814 (1995).