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The Editor.

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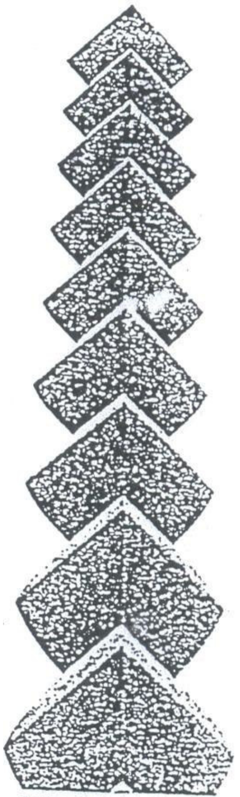

Endless Column, 1937, cast iron
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A TRIBUTE TO PROF. DR. FARUK JOSÉ NOME AGUILERA ON HIS 60th BIRTHDAY

Lavinel G. Ionescu [a,b], **Luis Alcides Brandini De Boni**[c] **and Eduardo Goldani**[c]

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ABSTRACT

Prof. Faruk José Nome Aguilera was born in Linares, Chile on May 29, 1947. He graduated in biochemistry from the University of Chile in 1971, obtained the Ph.D. Degree in Chemistry from Texas A& M University in 1976 and has been a faculty member at the Universidade Federal de Santa Catarina, Florianópolis, Brazil since 1977. His main research interests deal with catalysis and mechanisms of organic reactions in solution. He has trained approximately eighty research scientists including more than forty master and twenty doctoral students and has published about three hundred scientific articles. Prof. Faruk is a member of the Brazilian Academy of Science.

KEY WORDS : History of chemistry. Organic Reactions Mechanism, Science in Brazil

RESUMO

Prof. Faruk José Nome Aguilera nasceu em Linares, Chile em 29 de Maio de 1947. Ele se formou em bioquímica na Universidad de Chile e obteve o grau de Ph.D. em Química da Texas A&M University em 1976 e faz parte do corpo docente da Universidade Federal de Santa Catarina em Florianópolis, Brasil desde 1977. Suas atividades principais de pesquisa tratam de catálise e mecanismos de reações orgânicas em solução. Ele preparou mais de oitenta pesquisadores, incluindo mais de quarenta alunos de mestrado e vinte de dourado e publicou aproximadamente trezentos trabalhos científicos. O Prof. Faruk é membro da Academia Brasileira de Ciências.

PALAVRAS-CHAVE: História da Química, Mecanismo de reações orgânicas, Ciência no Brasil.

Faruk José Nome Aguilera was born in Linares, Chile on May 30, 1947. He was the youngest of eleven siblings, six boys and five girls.

His father, José Maria Nome Gonzalez, originally from Damascus, Syria, settled in Chile at the beginning of the last century (1910) and with time became a very successful merchant.

His mother, Mercedes Aguilera, a true matriarch, was a member of a well to do Chilean family from the Maule Region.

Prof. Faruk attended primary and secondary school in Linares and as a child and as the youngest brother received a lot of special attention from all his family.

Linares is a very pleasant city located in the Maule Region in the center of the country, on the fertile central plain, about 300 km south of Santiago and 50 km south of Talca. The Cordillera of the Andes is not far away to the east. It was founded by Ambrosio O'Higgins, Viceroy of Peru in 1794. At the present, it has a population of about 80,000 people and it is an active agricultural, industrial, commercial and service center. It is the home of the Artillery School of the Chilean Army. One of its main attractions is the Cathedral Church of San Ambrosio de Linares and its square. It was inspired by the Basilica of Santo Ambrosio, Milano, Italy, and among the monuments of the central square there are some lions that in the more distant past adorned the main square of Lima, Peru.

The city counts among its natives important statesmen, politicians, poets, writers, musicians, scientists and intellectuals. We mention in passing, Abate Molina (Juan Ignacio Molina), priest, naturalist and father of Chilean science; Pablo Neruda, famous poet and Noble Prize winner and two former presidents of the country, Carlos Ibañez del Campo and Arturo Alessandri Palma.

Prof. Faruk began studies at the University of Chile, Santiago at the age of sixteen and graduated in biochemistry in 1971. He continued his studies at the graduate level at Texas A&M University and obtained the Ph.D. Degree in Chemistry in 1976. His research advisor was Prof. Janos H. Fendler.

In 1977 Prof. Faruk Nome joined the faculty of Universidade Federal de Santa Catarina (UFSC), in Florianópolis, Brazil, where he is still active at the present time and holds the position of Full Professor of Chemistry.

During his 30-year tenure as Professor at the Federal University of Santa Catarina (UFSC), Dr. Faruk Nome participated of a wide number of committees and councils at the departmental, university, state and national levels. Among them we cite the Graduate Committee in Chemistry, Superior Council of Science and Technology of the State of Santa Catarina (FUNCITEC), Brazilian National Research Council (CNPq) and the Brazilian Commission for Improvement of Higher Education (CAPES).

PROF. DR. FARUK JOSÉ NOME AGUILERA

Prof. Faruk's main research interests deal with catalysis and mechanisms of organic reactions in solution. One aspect of his work involves the development of catalysts for the hydrolysis of phosphate and sulfate esters, as well as nucleic acids, amides and other esters of biological interest. Another aspect deals with the effect of colloidal aggregates and artificial enzymes on organic reactions in solution. In particular, he is interested in the effect of dendrimers, functional polymers and anionic, cationic, neutral and zwitterionic micelles on organic reactions with special emphasis on reaction rates, reactivity, equilibrium and incorporation of substrates.

We (LGI) first met Prof. Faruk Nome Aguilera in July of 1978, soon after our arrival in Florianópolis, where we went mainly with the purpose to help establish the Master Degree Program in Physical Chemistry. Soon afterwards we collaborated doing research work on micellar catalysis, decomposition of pesticides and micelle formation.

At the time, Prof. Faruk was a young and enthusiastic scientist, full of energy, dreams and expectations.

He had the option to return to his native Chile, set up a chemical laboratory in Linares, where his brothers reserved a whole floor of a tall building in the center of the town, be close to his family or accept a position as a faculty member at the University of Chile. He decided to stay in Florianópolis and be a pioneer in science in Santa Catarina.

The graduate program was not actually in Physical Chemistry. It consisted really of two programs under the same roof, one in Chemistry, the other in Physics. The Physics Department in Florianópolis, that was better established at the time, had all its plans for beginning a graduate program undermined by physicists at the Universidade Federal do Rio Grande do Sul (UFRGS) in Porto Alegre, who felt more comfortable without any competition in Southern Brazil.

During the initial stages of the program we mention the substantial and fundamental effort and contribution of Profs. John Dale Gault (USA), Ted Ray Taylor (USA), Subramania Jayaraman (India) and Joel Louis Rene Muzart (France) in Physics and Prof. Faruk (Chile), Juan Jacob Eduardo Humeres Allende (Chile) and ourself (LGI-USA) in Chemistry. A few years later we were joined by Prof. Rosendo Augusto Yunes from Argentina. The research activity in physics dealt mainly with liquid crystals and phase transitions and in chemistry with organic reactions, surfactants and micelles.

Among the Brazilians who were students in the beginning and later made significant contributions, we cite Profs. Ademir Neves, Bruno Szpoganicz, Eduardo Stadler and Eduardo Pinheiro in Chemistry and Luiz Taylor Silveira Siedler, Abio Valeriano de Andrades Pinto and Antônio Rogério de Souza in Physics. Worthy of special note are the efforts and contributions of Graça Hoeller, secretary of the Graduate Program from the beginning to the present and Jadir Caminatti who has been helping with administrative tasks since 1981.

The Graduate Program in Physical Chemistry terminated officially in 1991 with the simultaneous establishment of two separate Doctoral Programs, one in Chemistry and the other one in Physics. At the present, both of them are considered of excellent quality and are widely respected throughout Brazil. A total of one hundred ninety nine (199) master theses were approved during the duration of the Graduate Program in Physical Chemistry, more or less evenly divided between chemistry and physics

The new program in chemistry led to the graduation of two hundred and fifty eight (258) master students and one hundred and ninety three (193) doctoral students from 1990 to the present date.

In retrospect, it is relatively easy to see what Prof. Dr. Faruk José Nome Aguilera accomplished in thirty years of effort and hard work in Florianópolis, Brazil. We may only conjecture what might have happened if he had returned to his native Chile. Prof. Faruk Nome might have been a very successful businessman , owner of a chain of chemical laboratories scattered throughout Chile, widely respected scientist and educator or Minister of Education, Science

and Technology. He could have spent hundreds of weekends resting and reflecting at Pesce Rey, a mountain resort in the Andes, property of his family.

We salute Prof. Dr. Faruk José Nome Aguilera on the occasion of his sixtieth birthday, pay our modest tribute to him as a scientist, colleague and friend and congratulate him for his effort and accomplishments during the last thirty years and convey him the best wishes of good health, happiness and success for the days to come.

SOME REPRESENTATIVE PUBLICATIONS

1. **FERREIRA, V B N; BORTOLUZZI, A J; KIRBY, A J; NOME, F . 2-Allyloxy-5-chlorobenzoic acid. Acta Crystallographica. Section E, v. E63, p. o2981-02981, 2007.**
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HYDROLYSIS AND DEUTERATION OF GLYCYLGLYCINE CATALYZED BY DINUCLEAR $[BMXDCu_2]^{4+}$ COMPLEX

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ABSTRACT

Kinetic studies of hydrolysis and deuteration of glycylglycine by dinuclear $[BMXDCu_2]^{4+}$ *complexes were following by* NMR^1H. *Two parallel reactions were observed for the ternary system BMXD-*Cu_2*-Glycylglycine: peptide bond hydrolysis and* NCH_2 *deuteration reactions. The reaction rates show a first order behavior to the concentration of the ternary [BMXD*Cu_2*Glycylglycine] complex. The specific rate constants for the hydrolysis reaction are:* $k_{LCu_2HGG^{4+}}$ *(L = BMXD and GG = glycylglycine) =* $1{,}8 \times 10^{-6}\ s^{-1}$; $k_{LCu_2GG^{3+}} = 2{,}3 \times 10^{-6}\ s^{-1}$; $k_{LCu_2H_{-1}GG^{2+}}$, $k_{LCu_2(OH)H_{-1}GG^{+}}$ *and* $k_{LCu_2(OH)_2H_{-1}GG} = 0$, *and the specific deuteration rate constants for individual species are:* $k_{LCu_2HGG^{4+}} = 3{,}9 \times 10^{-6}\ s^{-1}$; $k_{LCu_2GG^{3+}} = 4{,}3 \times 10^{-6}\ s^{-1}$; $k_{LCu_2H_{-1}GG^{2+}}$, $k_{LCu_2(OH)H_{-1}GG^{+}}$ *and* $k_{LCu_2(OH)_2H_{-1}GG} = 0$. *The results show that the most active species toward hydrolysis and deuteration reactions are the protonated and non-protonated species, the former being the most reactive species. Semi-empirical calculations for energy minimization showed that the binuclear* $[BMXD\text{-}Cu_2]^{4+}$*) complexes adopt the boat-type conformation, in order to accommodate the dipeptide glycylglycine.*

KEYWORDS: hydrolysis; deuteration; dinuclear $[BMXD\text{-}Cu_2]^{4+}$ complexes, glycylglycine.

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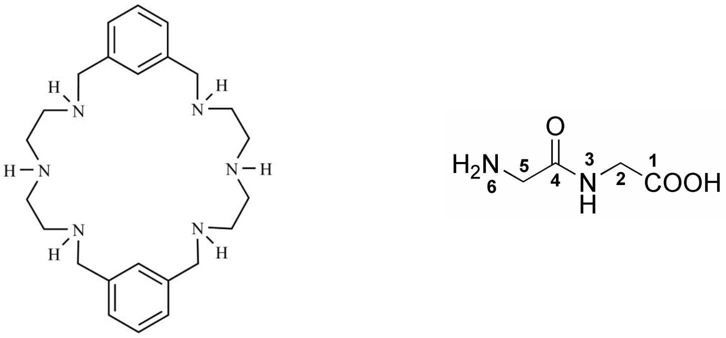
RESUMO

Estudos cinéticos da hidrólise e deuteração da glicilglicina pelo complexo binuclear $[BMXDCu_2]^{4+}$*foram acompanhados por NMR*^{1}*H. Duas reações paralelas foram detectadas para o sistema ternário BMXD-*Cu_2*-GG: reação de hidrólise da ligação peptídica e a deuteração do* NCH_2*. A velocidade de reação demonstra um comportamento de primeira ordem para o complexo ternário* $[BMXDCu_2GG]$*. As constantes de velocidade específicas para as reações de hidrólise são:* $k_{LCu_2HGG^{4+}}$ *(L = BMXD e GG = glicilglicina) = 1,8 x 10*$^{-6}$ *s*$^{-1}$*;* $k_{LCu_2GG^{3+}}$ *= 2,3 x 10*$^{-6}$ *s*$^{-1}$*;* $k_{LCu_2H_{-1}GG^{2+}}$, $k_{LCu_2(OH)H_{-1}GG^{+}}$ *e* $k_{LCu_2(OH)_2H_{-1}GG}$ *= 0, e as constantes de velocidade específicas para a reação de deuteração das espécies são:* $k_{LCu_2HGG^{4+}}$ *= 3,9 x 10*$^{-6}$ *s*$^{-1}$*;* $k_{LCu_2GG^{3+}}$ *= 4,3 x 10*$^{-6}$ *s*$^{-1}$*;* $k_{LCu_2H_{-1}GG^{2+}}$, $k_{LCu_2(OH)H_{-1}GG^{+}}$ *e* $k_{LCu_2(OH)_2H_{-1}GG}$ *= 0. Os resultados demonstram que as espécies ativas para as reações de hidrólise e deuteração são a protonada e a não-protonada. Cálculos semi-empíricos para minimização de energia mostram que o complexo binuclear* $[BMXDCu_2]^{4+}$ *adota a conformação do tipo "cuia" para acomodar o dipeptídeo glicilglicina.*

1. INTRODUCTION

Macrocyclic ligands containing two chelating subunits linked by two bridges may form both mononuclear and dinuclear complexes with metal cations.[1] Of special interest among this growing body of complexing agents are the macrocyclic ligands because they can impose a high degree of preorganization on metal complex formation.[2] The hexamine 3,6,9,17,23–hexaazatricyclo [23.3.1.1] triaconta 1(29), 11(30), 12, 14, 25, 27-hexaene (L) (Figure 1), is a ligand with considerable flexibility, that forms a dinuclear arrangement by inclusion of two cations in its molecular cavity, leaving additional coordination sites in the metals available.[3] The structure of dinuclear copper(II) complex of BMXD was determined by X-ray methods, showing that BMXD adopts preferred spatial configurations dependent on the substrate coordinated in its cavity.[3] Basallote and co-workers published kinetic studies of formation of mono- and dinuclear copper(II) complexes with ligand BMXD under slightly acidic solutions[4] and extremely basic solutions.[5]



BMXD **Glycylglycine**

Figure 1. Formulas of ligand BMXD and dipeptide Glycylglycine

Many biological processes involve the hydrolysis of proteins and peptides[6] and it has been shown that metal complexes of dinuclear macrocyclic ligands may also serve as models for certain metalloproteins that require the presence of two metal centers for activity.[7] Copper(II) ion catalysis of the hydrolysis of glycylglycine has been reported.[8] Hydrolysis of glycylglycine (Figure 1) by a mononuclear macrocyclic copper(II) complex, Cu[9]aneN_3Cl_2, has been reported using a catalytic process.[9] In agreement with Bordignon-Luiz [10], the dinuclear macrocyclic complex $[OBISDIENCu_2]^{4+}$ was proposed as a catalyst to the glycylglycine hydrolysis; the reaction was studied at various pD values (pD = $-\log[D^+]$) and the glycine was the observed product.

In this paper, kinetic studies of ternary system BMXD-Cu_2-GG are reported and a mechanism is proposed for hydrolysis and deuteration of glycylglycine catalyzed by dinuclear $[BMXDCu_2]^{4+}$ complexes. A spatial conformation of BMXD-Cu_2-GG system is presented, with the aid of the calculations based on minimization of potential energy.

2. EXPERIMENTAL

BMXD was synthesized by a method described in the literature.[11] Glycylglycine (Aldrich) was reagent grade material and was used without further purification. A stock solution of Cu(II) chloride dihydrate ($CuCl_2.2H_2O$ – Vetec) was standardized by titration with EDTA (ethylenediamine-tetraacetic acid – Vetec) with murexide as the indicator.[12] Deuterated water (D_2O 99% - Acros Organics) and a solution of deuterated sodium hydroxide, NaOD 30t% wt in D_2O (Aldrich), were used to prepare the experimental solutions utilized in the H-NMR experiments.

2.1. NMR Measurements

The NMR spectra of the compounds in 99% D_2O were recorded with a 200MHz Bruker AC 200 Spectrometer at 25.0ºC. Internal reference was sodium 3-trimethylsilylpropanesulfonate (DSS), and the water peak was also used as a reference. Sample solutions with various pD values were prepared by adding a NaOD/D_2O solution that was prepared from a 30% wt/wt solution in 99% D_2O. The concentration of the system was ca. 0.01 mol L^{-1} BMXD, 0.02 mol L^{-1} Cu(II) and 0.01- 0.03 mol L^{-1} glycylglycine. The pD values of the solutions were measured by using a Micronal B-474 pH meter equipped with a combination electrode (Ingold). The instrument was standardized with diluted HCl solutions and the readings were converted to pD by the relation $pD = pH_{meas.} + 0.40$ [13], and the pD of the reaction was maintained constant with additions of small amounts of concentrated NaOD with a Gilmon burette. The solutions were incubated in a 70.0 ± 0.1ºC constant temperature bath (Etica Equipments Cientifics S.A.). The kinetics reactions were carried out at 70.0ºC because they are very slow at 25.0ºC.

The values of k_{obs} were calculated by following the disappearance of the NCH_2 (CH_2 adjacent to the amino group, C5, Figure 1), and the CCH_2 resonance (CH_2 adjacent to the carboxyl group, C2) when possible. Since the reaction was slow, the integrations of the resonances were normalized with respect to the CH_2 resonances of the macrocycle.

2.2. Characterization of Hydrolysis Product

The hydrolysis product was characterized by H-NMR. The experimental solutions were allowed to react and after an interval of time copper(II) ion were precipitated with H_2S generated from the reaction of iron(II) sulfide and concentrated HCl. The suspension was then centrifuged (Centrifuge Excelsa Baby II – Model 206-R, Fanem).

2.3. Calculation Method

Using semi-empiric models, where only the valence electrons of the atoms are considered, lower energy conformations were obtained for the complexes $[BMXDCu_2]^{4+}$

and $[BMXDCu_2]^{4+}$ + Glycylglycine. The calculation of energy minimization was carried out with the program CAChe[14] (Computer-Aided Chemistry) version 5.0 (Fujitsu), using the AM1-d[15] (Austin Model 1) as parametrization method, and with the EF[16] (Eigenvector Following) as the optimization model.

3. RESULTS AND DISCUSSION

3.1.Kinetic Measurements

Equilibrium studies of BMXD-Cu_2-GG system had been previously carried out, and the stability constants[17] was used with a different concentrations of reagents to generate a species distribution plot[18] (Figure 2), which was used to select the appropriate conditions to perform kinetic runs. Two parallel reactions were observed: hydrolysis of peptide bond and deuteration of NCH_2 (CH_2 adjacent to the amino group).

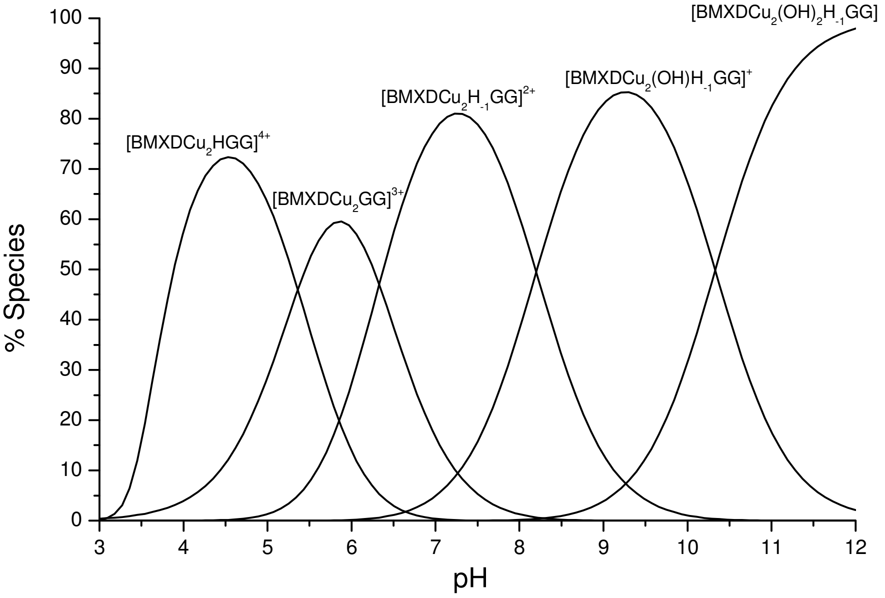


Figure 2. Species distribution curves of BMXD-Cu_2-GG system as a function of pH. [BMXD]=1.00 × 10^{-2} $molL^{-1}$; [Cu(II)]=2.00 × 10^{-2} $molL^{-1}$; [GG]=1.00 × 10^{-2} $molL^{-1}$; μ = 0,100 $molL^{-1}$ (KCl).

The proton NMR spectra of the BMXD-Cu_2-GG system at pD 6.1 (Figure 3) shows a resonance at 3.80 ppm due to the CH_2 adjacent to the amino group, and a resonance at

3.89 ppm due to the CH_2 adjacent to the carboxylate group of glycylglycine. The deuteration reactions were studied following the sequence I, II, III, shown in Figure. 3. Deuteration occurs at the NCH_2 of the peptide, while the CCH_2 does not deuterate under these conditions. The product appears at 3.62 ppm as a singlet. Deuteration of some peptides has been reported previously and was found to occur at the NCH_2 group.[10,19]

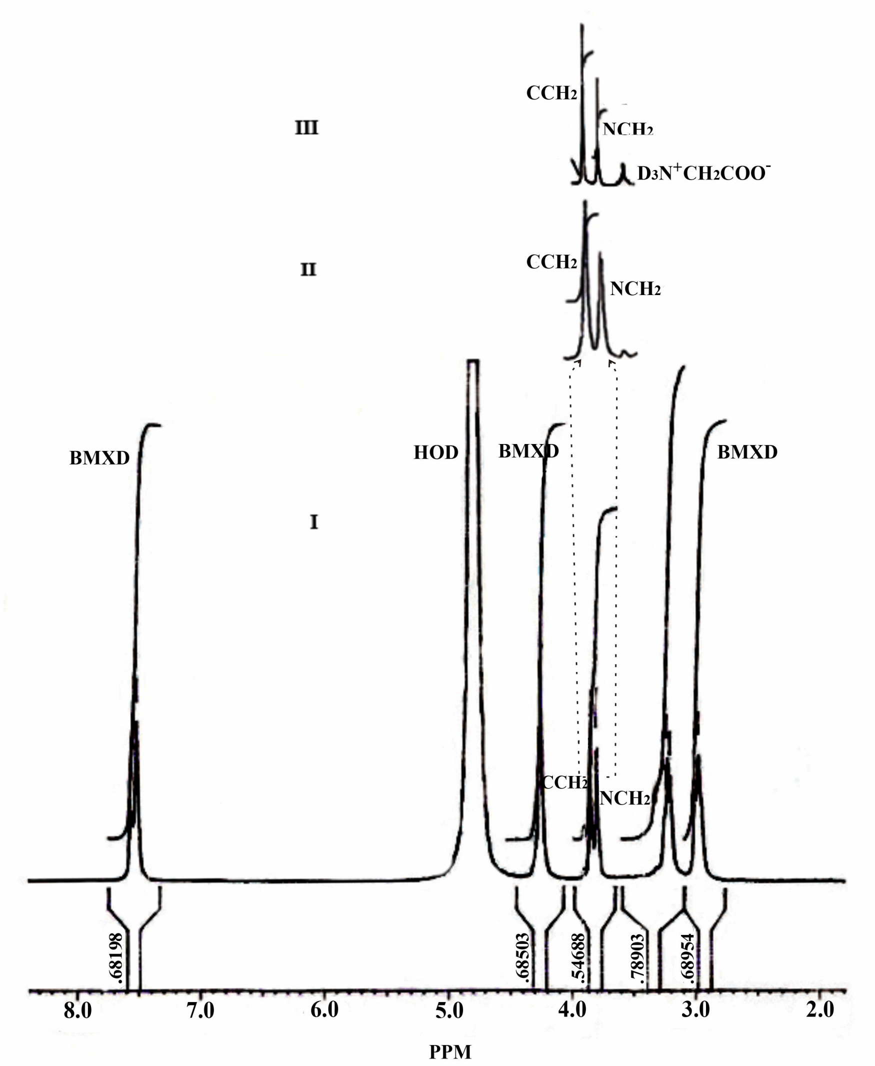


Figure 3. Selected 200 MHz proton NMR spectra of the 1:2:1 BMXD-Cu_2-GG system for a solution initially containing 1.00 x 10^{-2} $molL^{-1}$ BMXD, 2.00 x 10^{-2} $molL^{-1}$ Cu(II) and 1.00 x 10^{-2} $molL^{-1}$ GG at pD 6.1, showing the decrease in the signal and resonance due to glycylglycine CH_2 protons; (I) = initial; (II) = after 50 h and (III) = after 72 h in D_2O; T = 70.0 ± 0.1°C and μ = 0.100 $molL^{-1}$ (KCl).

The kinetic results are interpreted with Equations (1) and (2).

$$\text{glycylglycine} \xrightarrow{k_h} 2\ \text{glycine} \quad (1)$$

$$\text{glycylglycine} \xrightarrow{k_d} \text{deuterated glycylglycine} \quad (2)$$

where k_h is the hydrolysis constant and k_d is the deuteration constant. The observed rate constant is the sum of these two constants, Equation (3).

$$k_{obs} = k_h + k_d \quad (3)$$

The disappearance of the NCH_2 resonance with time was measured to calculate the values of k_{obs}. The observed rate constants were calculated from the straight-line slope of $\ln[NCH_2]$ versus time (Figure 4). The hydrolysis constants were calculated with the aid of Equation (4)[20] and the values of the deuterated constants, k_d, were determined with the aid of Equation (3) and are listed in Table 1.

$$[GG] = \frac{k_h\,[GG]_0\,(1 - e^{-k_{obs}t})}{k_{obs}} \quad (4)$$

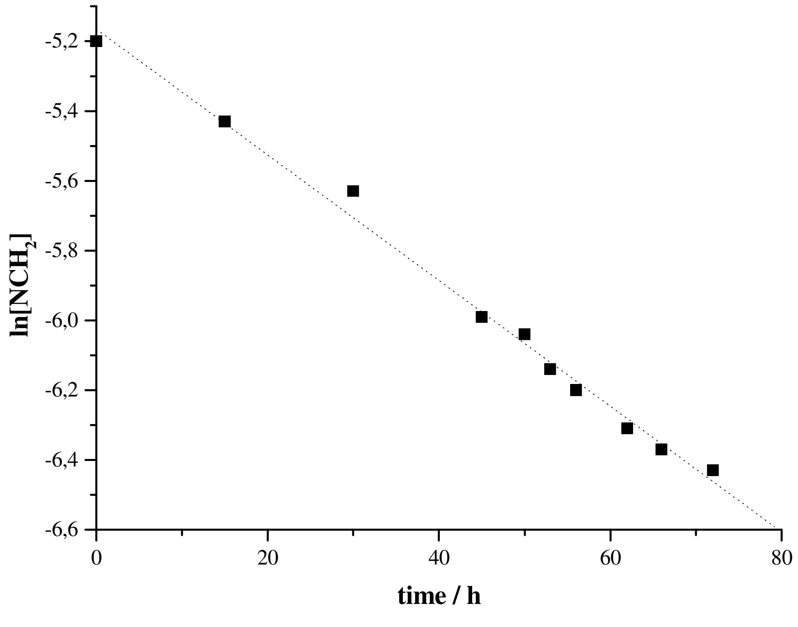


Figure 4. Plot of $\ln[NCH_2]$ vs. time for the deuteration and hydrolysis of CH_2 adjacent to the amino group of the dipeptide glycylglycine in D_2O at pD 6.1, $t = 70.0 \pm 0.1°C$ and $\mu = 0.100\ molL^{-1}$ (KCl).

Table 1. Observed deuteration and hydrolysis constants for glycylglycine (T = 70.0 ± 0.1°C and $\mu = 0.100$ molL^{-1} KCl)

pD	k_{obs} (10^{-6} s^{-1})	k_h (10^{-6} s^{-1})	k_d (10^{-6} s^{-1})
4,5	3.3(2)	0.9(2)	2.4(2)
6,1	5.0(1)	1.6(1)	3.4(1)
7,1	1.5(2)	0.5(2)	1.0(3)
8,0	0	0	0
10,4	0	0	0

The numbers in parentheses are the estimated errors in the last significant figure.

The hydrolysis constants were calculated independently of deuteration by following the disappearance of the CCH_2 resonance in the proton NMR spectrum, illustrated in Figure 5. In this way the hydrolysis is independent of deuteration, since both species, deuterated and non deuterated glycylglycine, undergo hydrolysis. The CCH_2 group is the CH_2 adjacent to the carboxylic group of glycylglycine.

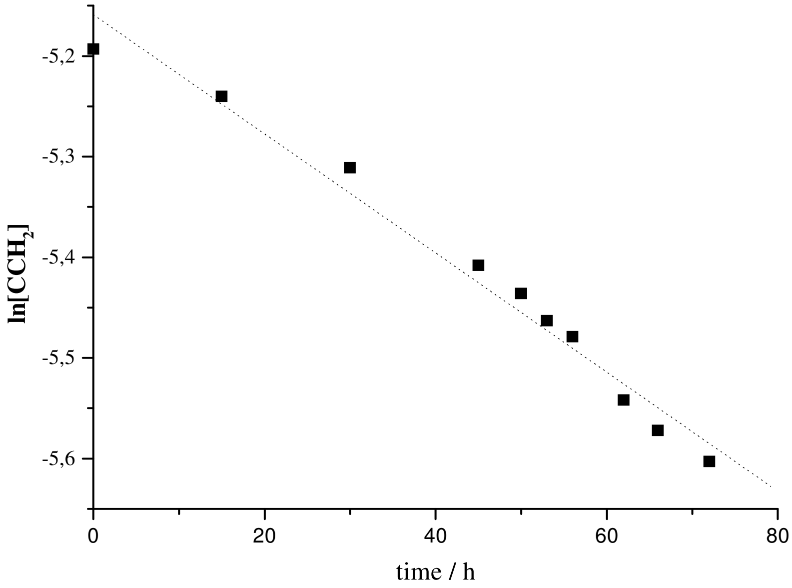


Figure 5. Plot of ln[CCH_2] vs. time for the hydrolysis of the dipeptide glycylglycine in D_2O at pD 6.1, T = 70.0 ± 0.1°C and $\mu = 0.100$ molL^{-1} (KCl).

The specific rate constants for the hydrolysis reaction for each active species present in the system were calculated with Equation (5), and the concentrations of each species were obtained from Figure 2. The species distribution curves at 25.0ºC were used in this study, because it was not possible to carry out the equilibrium studies at 70 ºC because the reactions occur at this temperature. The equilibrium constants are not expected to change substantially with a 45.0ºC temperature variation.

$$k_h[LCu_2GG]_T=k_1[LCu_2HGG^{4+}]+k_2[LCu_2GG^{3+}]+k_3[LCu_2H_{-1}GG^{2+}]+k_4[LCu_2(OH)H_{-1}GG^{+}]+ k_5[LCu_2(OH)_2H_{-1}GG] \qquad (5)$$

$[LCu_2GG]_T$ is the total concentration of species in the BMXD-Cu(II)-GG system, and k_1, k_2, k_3, k_4 and k_5 are the specific hydrolysis constants of each species: monoprotonated, non-protonated, amide deprotonated, monohydroxide and dihydroxide species, respectively. The values of specific rate constants determined for these species are given in Table 2.

Table 2. Specific hydrolysis and deuteration rate constants of N-terminal CH_2 residue of glycylglycine (T = 70.0 ± 0.1°C and μ = 0.100 mol L^{-1} KCl)

Species	k_h (10^{-6} s^{-1}) (hydrolysis)	k_d (10^{-6} s^{-1}) (deuteration)
LCu_2HGG^{4+}	1.8(6)	3.9(4)
LCu_2GG^{3+}	2.3(1)	4.3(1)
$LCu_2H_{-1}GG^{2+}$	0	0
$LCu_2(OH)H_{-1}GG^{+}$	0	0
$LCu_2(OH)_2H_{-1}GG$	0	0

The numbers in parentheses are the estimated errors in the last significant figure.

The most active species with regard to the hydrolysis reaction is the non-protonated species. Deprotonation of amide bond stabilizes the peptide bond in relation to the hydrolysis reaction, and the specific rate constants for the amide deprotonated and the two hydroxo species (which are also amide deprotonated) indicate zero activity or too low to be measured with the method employed.

The same method of calculation was carried out for the deuteration reaction and the specific deuteration rate constants were calculated with the aid of Equation 6, which is similar to Equation 5. The most active species is also the non protonated species, which is to be expected since both reactions have the same intermediate, a ternary dinuclear BMXD-Cu(II) glycylglycine complex.

$$k_d[LCu_2GG]_T=k_1[LCu_2HGG^{4+}]+k_2[LCu_2GG^{3+}]+k_3[LCu_2H_{-1}GG^{2+}]+k_4[LCu_2(OH)H_{-1}GG^{+}]+ k_5[LCu_2(OH)_2H_{-1}GG] \quad (6)$$

3.2.Semi-Empirical Calculation

Theoretical results showed that the macrocycle structure loses degrees of freedom in its conformation when the copper II take its place in the structure, as can be seen in the Figure 6 (top view). Although the binuclear macrocycle complex $[BMXDCu_2]^{4+}$ has a more rigid structure, being more symmetrical, the complex appears to be able to be adapted, depending on the ligand that is complexed. Calculations involving one and two hydroxyl groups, as well as water molecules, were used to address these considerations. Thus, depending on the substrate coordinated in the macrocycle cavity, variations in the distance of the copper (II) atoms are observed.

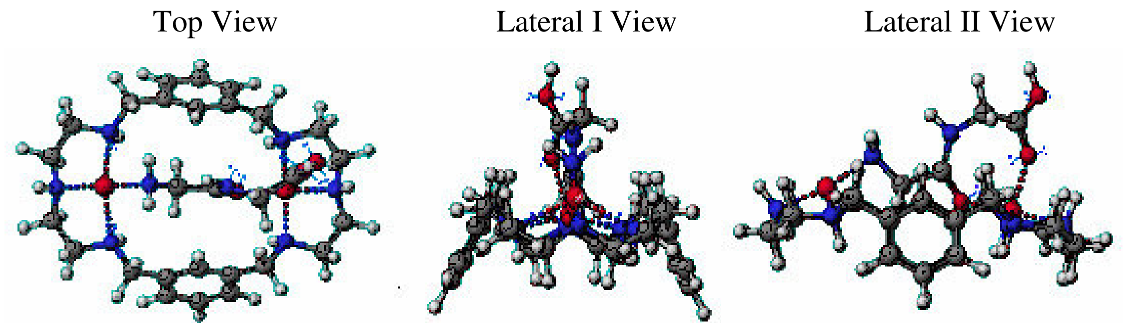


Figure 6. Conformations of low energy of the complex $[BMXDCu_2]^{4+}$.

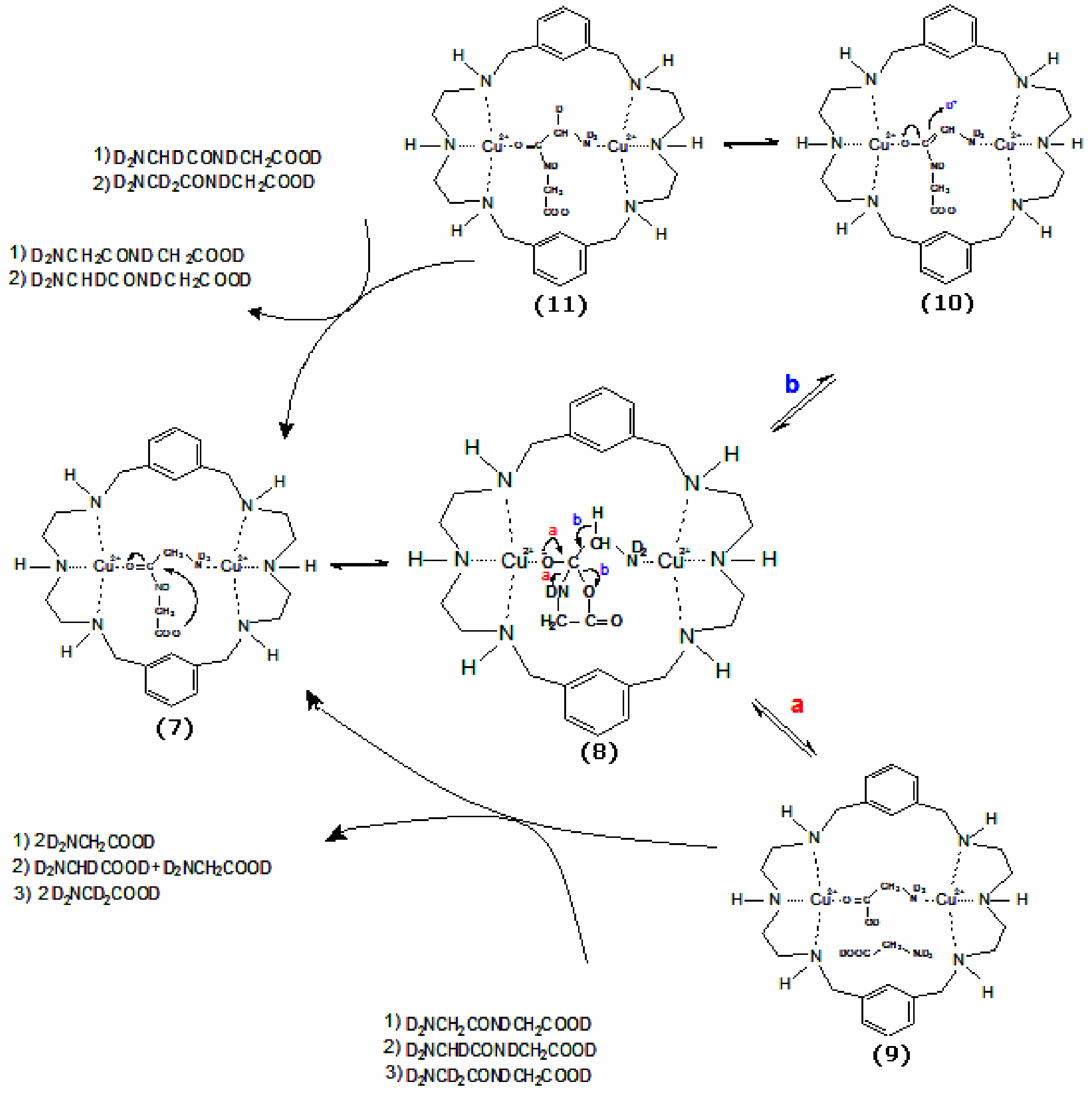
The molecule presents certain symmetry, where the aromatic rings are moved to the bottom, and the two diethylenotriamine subunits are turned to the same side, characterizing a "boat" type conformation. The inter-atomic distance of the two copper (II) centers is 6.9 Å.

The glycylglycine must approach the complex at the top, since underneath there is a large steric hindrance, due to the nuclei of the atoms involved, and also due to an electronic steric hindrance, as this area is already occupied by many electrons (aromatic rings).

As previously mentioned, even though the minimization calculations reproduce the complex $[BMXDCu_2GG]^{2+}$ structure, showing that the macrocycle adopts the "boat" type conformation, this is not necessarily the structure that the complex would adopt in solution, since the calculations did not consider the relationship of these structures with molecules or potentials that would characterize a solvent interaction.

4. Conclusion

The proposed mechanism for dinuclear $[BMXDCu_2]^{4+}$ catalyzed hydrolysis and deuteration reactions of glycylglycine can be seen in Scheme 1. Coordination of glycylglycine in the cavity of the "host" complex BMXD-dicopper(II) yields the ternary complex 7 (Scheme 1). In this complex, the amino group is coordinated to the Cu(II) ion on one side, and the amide carbonyl is labilized by the metal center on the other side of the dinuclear $[BMXDCu_2]^{4+}$ complex, allowing a nucleophilic attack by the carboxylate group of the dipeptide. The reactions are first-order in the ternary complex concentration, since they depend on the intramolecular attack of the terminal carboxylate group on the amide carbonyl, yielding a cyclic intermediate (8), as required for the two parallel reactions: hydrolysis of the peptide bond and deuteration of NCH_2 group. The hydrolysis reaction follows the path "a" and the breaking of the C-N bond yields the intermediate anhydride. The anhydride intermediate undergoes a fast nucleophilic attack, yielding (9) and two glycine molecules. The coordination of a new glycylglycine molecule closes the catalytic cycle.



The deuteration reaction follows path “b”. Deuteration of intermediate (10) yields a monodeuterated molecule of glycylglycine (11), which may be substituted by a new molecule of the dipeptide, closing the catalytic cycle. The two cycles occur in parallel producing deuterated and non deuterated glycine molecules.

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THE PERIODIC TABLE OF THE ELEMENTS AND THE ASSOCIATED MINERALS: GOLD

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ABSTRACT

Gold is a natural solid with a crystalline stable structure and exhibits an abundance of 0.04 ppm (mg/Kg) in the Earth crust. Gold, like silver, is one of the chemical elements less abundant in nature. Only palladium, tellurium, platinum, ruthenium, rhodium, osmium, rhenium, and iridium, present a smaller geochemical distribution. Because of its low chemical reactivity, the metal has very few minerals. This review presents a synopsis of the twenty nine (29) gold minerals known at the present time.

KEY WORDS: gold, mineralogy of gold, uses of gold.

RESUMO

O ouro é um sólido natural que apresenta estrutura cristalina estável e, que ocorre com uma distribuição geoquímica de apenas 0,04 ppm (mg/Kg) na crosta terrestre. Somente o paládio, o telúrio, a platina, o rutênio, o ródio, o ósmio, o rênio e o irídio apresentam uma distribuição menor. Isso se deve à baixa reatividade química do metal, responsável pela sua pouca representatividade na constituição dos minerais. Este trabalho apresenta uma rápida sinopse dos vinte e nove (29) minerais nos quais o ouro encontra-se presente, conhecidos até o momento.

PALAVRAS-CHAVE: ouro, mineralogia do ouro, uso do ouro.

INTRODUCTION

Like silver, gold is one of the chemical elements less abundant in the Earth's crust. Only palladium, tellurium, osmium, rhenium and iridium have a lower geochemical distribution[1-3,16].

Gold (Au, from the Latin, *aurum*), is a soft, heavy, yellow metal that melts at 1064,43°C. It is the most malleable and ductile of all metals. Generally speaking, gold is chemically unreactive and is not attacked by oxygen or sulfur. It is not attacked by individual acids but, reacts readily with halogens or with solutions containing chlorine. For example, a mixture of nitric and hydrochloric acids (aqua regia) generating chlorine leads to the formation of auric chloride ($AuCI_3$). Gold dissolves in cyanide solutions in the presence of air or hydrogen peroxide to form $Au(CN)_2^-$. The reduction of solutions of $AuCI_4$ by various reducing agents such as $SnCl_3^-$, gives under suitable conditions highly colored solutions containing colloidal gold. Like silver, gold forms many alloys and some can be regarded as compounds, e.g. Cs^+Au^- and $AuTe_2$. Gold also forms many stable gaseous molecules like AlAu and NiAu[8-10].

As a metal of the Group 11 it has the following periodical properties: Z = 79; Symbol Au; A = 196.967 u; Atomic ray = 1.46 A^0; Ionic ray = 1.37 A^0; Eletronic configuration n = [Xe] $4f^{14}5d^{10}6s^1$; Melting point = 1,064 ^0C; Boiling point = 2,808 ^0C; Termal conductivity = 0.758 cal.cm/seg.^0C cm^{-2}; Electric resistivity 2.35 micron-ohm.cm at 20 ^0C; Oxidation states 0, I, III, and V; Reduction potential = 1.68 volts; and Density = 19.32 g cm[8,14].The industrial use of gold consists mainly of jewelry alloys (intermetallic alloys of Ag and Cu), international monetary standard, and electric contacts[8]. The most common gold minerals used as industrial sources are: native gold, calaverite, krennerite, nagyagite, petzite, and sylvanite[2]. Gold can also be obtained as subproduct of Cu-Pb-Zn mineralization. Other gold minerals are used for scientific purposes, and collections. Gold minerals are usually sulfides and similar compounds (14 species), intermetallic alloys (10 species), sulfossalts (4 species), and native element (1 specie). Its distribution in minerals are: silicates 0.0002 – 0.924 ppm; native elements (Ag, Pd, Pt, Cu, Te, As, Sb, S) 1000 ppm; sulfides and similar compounds 500 ppm; and jarosite $KFe_3(SO_4)_2(OH)_6$ 7900 ppm[1].

Although Au is sometimes found in small lumps or nuggets or in alluvial sands and gravels, it is more often associated with ores of silver, copper, lead and zinc. Gold is found in two major type deposits. Lode deposits are deposits where gold is found in cracks and veins in rocks. The second type of gold deposit is called a placer deposit. Placer deposits are formed when moving water eroded gold out of vein deposits or rocks-hosted disseminated gold. When the speed of water in the river slows down, the heavy gold falls to the bottom of the riverbed and accumulates in the sand and gravel. A third major source of gold is the recovery of the precious metal as subproduct of copper and silver mining[15].

The total amount of gold yet to be retrieved from the Earth is estimated at 100,000 tons. Republic of South Africa is the world's largest gold producer and holds about half of the reserves. The United States and Brazil possess significant amounts of the rest of the world's gold resources. About one fifth of the total resources of gold in the world is a component of copper and silver ores[1,2].

Gold in alluvial deposits is separated from the altered rocky matter, or sediment by washing with water. Because of its great density, gold sinks to the bottom while the earth deposits are washed away[22].

Mercury is used to remove the gold from ores by forming an amalgam from which mercury is subsequently distilled, The amalgamation process on an industrial scale was first developed in Zacatecas, Mexico by Bartolomé de Medina in 1555 for the extraction of silver[13].

Chlorine gas and sodium cyanide are also used to extract gold by different processes. Gold may be purified by electrolysis, as is the case with copper.

Gold is an element known, worked and appreciated by man since ancient times. It has always been considered a symbol of wealth and is cited repeatedly in the book of Genesis.

Apparently, the earliest mining activities occurred about 4000 B.C. in present day Romania and Bulgaria[9-13], inhabited at the time by the Thracians. Their refined taste for gold decorative objects is well attested by the Thesaurus of Pietroasa, Thesaurus of Sãncrãieni and the vast quantity of jewelry found in the tombs of Thracian kings near Vama and many other places in this part of Eastern Europe. The gold was obtained from mines in the Southern Carpathians (Transylvanian Alps) and the Mount Pangaion Region in Thrace. Unshorn sheepskin was used to recover gold dust from river sands on the shores of the Black Sea and this practice most likely 100 to the inspiration of the legend of the Golden Fleece[9-12].

During about the same period, extensive mining of gold also took place in ancient Egypt, particularly Nubia (present day Sudan). The Egyptians mastered the art of alloying gold with copper, the art of beating gold into leaf to extend its use and started casting gold using the lost-wax technique. The Egyptians cast and used the first standardized gold bars as means of payment and the Shekel, a coin originally weighing 11,3 grams became a standard unit of measure. It contained a naturally occurring alloy called *electrum* that was approximately two-thirds gold and one-third silver. As far as is known, Alchemy also originated later (about 300 B.C.) in Alexandria, Egypt and besides the elixir of long life and the philosopher's stone, the alchemists' main quest was to turn base metals into gold.

Most peoples throughout history adopted gold coins for their monetary systems. During the ancient times, we mention the Macedonians under Alexander the Great, the Romans and the Chinese. During more recent times, we cite the Arabs, the Italian (Florence, Genoa and Venice), England, France, Spain, the United States and many other countries. The best known golden coins were the Aureus (Rome), Ducat (Venice), Florin (Great Britain) and the Krugerrand (Republic of South Africa). Eventually, gold became a universal monetary standard[10].

During the Second Punic War with Carthage (202 B.C.), the Romans gained access to the gold mining region of Spain (*Saguntum*) and recovered gold from stream gravels and sands and by hard rock mining. At the end of the campaign in Gaul (58 B.C.), Julius Cesar brought back enough gold to give 200 coins to each of his soldiers and repay all of Rome's debts.

After the conquest of Dacia (present day Romania) by Emperor Traianus (106 A.D.), special attention was given to the mining of gold in the new province. The

mines became property of the Emperor and the Chief Mining Officer was called *Procurator Aurarium*. There were twelve mines in complete operation at the time, mostly in the Metaliferi Mountains, not far from the Dacian capital of *Sarmisegetusa* (*Ulpia Traiana*)[11,12]. The extraction of gold was done by crushing hard rock, followed by washing with water or by recovery from river sands.

The approximate gold consumption during the past years range between 100 and 1300 tons per annum. The greatest demand come from the carat jewelry and varies on the average between 800 and 1000 tons per year. The rest of the consumption of gold fabrication, in approximate numbers is as follows: electronics (100 tons), official coins (100 tons), dentistry and medicine (50 tons), metals, medallions, fake coins (15 tons) and other industrial and decorative uses (50 tons).

Gold and gold salts have been used from the treatment of rheumatoid arthritis. Gold alloyed with nickel has been employed in the production of heat resistant bronzing alloys for the aerospace industry. Gold coated visors area a standard safety feature for astronaut excursions and Col. Edward White made the first space walk during the Gemini Mission in 1965 using a gold coated visor to protect his eyes from direct sunlight.

The Mars Global Surveyor, launched in 1996 had on board a gold coated parabolic telescope that generated a detailed map of the entire Martian surface. Astronomers at the Keck Observatory in Hawaii used giant gold coated mirrors and obtained very detailed images of Neptune and Uranus in 2000. Gold coated compact discs were introduced in 1986. They provide perfection of reflective surfaces, eliminate pinholes common to aluminum surfaces to exclude any possibility of oxidative deterioration of the surfaces.

In 1960 AT&T Bell Laboratories was granted the first patent for the invention of the laser. The device used very well positioned gold coated mirror to maximize infrared reflection into the lasing crystal. Eight years later INTEL introduced a microship with 1,024 transistors interconnected with invisibly small gold circuits.

In 1970 a charge-coupled device was invented at Bell Telephone Laboratories. It was originally employed to record faint light from stars using gold to collect the electrons generated by light. At the present time, the device is used in hundreds of civilian and military devices, including home video cameras[10].

In 1971 the colloidal gold marker system was introduced by Amersham Corporation. It used tiny spheres of gold to mark or tag specific proteins in the human body.

The first space shuttle, launched in 1981 used gold coated impellers in its liquid hydrogen fuel pump.

A new gold alloy 990 Gold (1 percent titanium) was introduced to meet the need for an improved durability of 99 percent pure gold. The new alloy is very malleable, can be worked into intricate design, but can also be converted into a hard, durable alloy by simple heating in an oven.

Because of its scarcity and low reactivity, gold forms a small number of minerals. At the present there are only twenty nine (29) gold minerals recognized by the International Mineralogical Association (IMA)[4].

Two minerals have been validated only recently, the sulfosalt Museumite, Pb_5AuSb_{12} whose typical section is from the gold-tellurite deposit of Săcărâmb,

Hunedoara County, Metaliferi Mountains, Romania[39,40] and Novodneprite, $AuPb_3$, an intermetallic alloy, whose typical section is from Novodneprovsk, Kazakhstan[7,15].

The majority of gold minerals are sulfides (principally tellurides) and intermetallic alloy classes, originated by hydrothermal processes in ore veins[19].

The main gold producers on a global scale are: USA, Russia, Canada, and Republic of South Africa. The countries with major bulk reserves are: Brazil, Australia, People's Republic of China, and Russia. Brazil contains important auriferous deposites in Serra Pelada (Pará) and Alta Floresta (Pará and Mato Grosso States)[2,56].

GOLD MINERALS

1. Anyuiite $Au(Pb,Sb)_2$ – Tetragonal System; Native Elements and alloys-metals Class; (Mwt = 568.64 g/mol (D); 10.71% Sb, 54.66% Pb and 34.64% Au); Type locality: Bolshoi Anyu River Basin, Magadan Region, Russia; the name was proposed in reference to the Anyui river, a site where the mineral was firstly found. Paragenesis: mineral of dunite-harzgurgite rocks, associated with ilmenite, magnetite (rich in Ti), spinel (rich in Cr), hematite, pyrite, chalcopyrite and apatite. Principal occurrences: Russia, People's Republic of China, Poland, New Zealand and Australia[4,17].

2. Auricupride Cu_3Au – Cubic System; Native Elements and alloys-metals Class; (Mwt = 387.60 g/mol; 49.18% Cu and 50.82% Au); Type locality: Zolotaya Gora (Golden Mount) deposit, Karabash, Chelyabinsk, South Urals, Siberia, Russia; named after its composition of Au and Cu. Paragenesis: typical mineral of serpentinites, associated with barite, chalcopyrite, chrysocolla, copper, cuprite, native gold, lead, magnetite, pyrite, quartz, tetra-auricupride, titanite and ullmannite. Principal occurrences: Russia, Republic of South Africa, Chile, Czech Republic and Brazil (Jacuí-Bom Jesus da Penha, Minas Gerais)[4,5,18,19,31,].

3. Aurostibite $AuSb_2$ – Cubic System; Sulfide (Antimonide) Class; (Mwt = 440.47 g/mol; 55.28% Sb and 44.72% Au); Type locality: Giant Yellowknife mine; Northwest Territories, Canada; Pyrite group; named after its composition of Sb and Au. Paragenesis: mineral found in hydrothermal gold-quartz veins, in portions deficient in sufur and contain Sb minerals, associated with arsenopyrite, calcite, native gold, pyrite, quartz, stibinite, freibergite, jamesonite, bournonite, boulangerite, chalcopyrite, berthierite and native antimony. Principal occurrences: Canada, Czech Republic, Australia, Finland, Norway, France, Germany, Ghana, Zimbabwe, Russia, Kazakhstan, People's Republic of China, Republic of South Africa, Bolivia and USA[4,20,21].

4. Bezsmertnovite $Au_4Cu(Te,Pb)$ – Orthorhombic System; Sulfide (Telluride) Class; (Mwt = 1,002.89 g/mol; 6,34% Cu, 8.91% Te, 6.20% Pb and 78.56% Au); Type locality: Aginskoye gold deposit, Kamchatka Peninsula, Russia; the name is a homage

to the Russian geologists Marianna Bezsmertnaya (1915 - 1991) and Valdir Bezsmertny. Paragenesis: mineral of the cementation zone of a volcanogenic gold telluride deposit, associated with balyakite, bilibinskite, bogdanovite, chalcopyrite, native gold, quartz, sylvanite, native tellurium and tetrahedrite. Principal occurrence: Russia[4,23].

5. Bilibinskite $Au_5Cu_3(Te,Pb)_5$ – Cubic (?) System; Sulfide (Telluride) Class; (Mwt = 1,180.39 g/mol; 10.77 Cu, 21.62% Te, 17.55% Pb and 50.06% Au); Type localities: Aginskoye gold deposit, Kamchatka Peninsula, Russia; Dzhelambert, Kazakhstan; named is a homage to the Russian geologist Yuri Bilibin (1902 - 1952). Paragenesis: mineral of the weathering of gold-telluride deposits, associated with bezsmertnovite, bogdanovite, tellurides of Au, Cu, Pb and Fe, native gold, and replacing krennerite and sylvanite. Principal occurrences: Russia and Kazakhstan[4,24].

6. Bogdanovite (Au,TePb)3(CuFe) – Cubic System; Native Elements and alloys-metals Class; (Mwt = 592.69 g/mol; 3.20% Fe, 7.08% Cu, 21.53% Te, 34.96 % Pb and 33.23% Au); Type locality: Aginskoye gold deposit, Kamchatka Peninsula, Russia; named is a homage to the Russian geologist Aleksei Bogdanov. Paragenesis: mineral of the oxidation zone of Au-Te deposits, associated with bilibinskite, bezsmertnovite, chalcopyrite, gold, sylvanite, tellurium. Principal occurrences: Russia, Kazakhstan, Mexico and USA[4,25,26].

7. Buckhornite $AuPb_2BiTe_2S_3$ – Orthorhombic System; Sulfide (Telluride) Class; Sulfosalt; (Mwt = 1,171.74 g/mol; 17.83% Bi, 21.78% Te, 35.37% Pb, 16.81 % Au and 8.21 % S); Type locality: Buckhorn Mine, Jamestown, Boulder County, Colorado, USA; named after its locality. Paragenesis: occur in quartz-carbonate veins, associated with gold, pyrite and tetradymite. Principal occurrences: USA, Armenia and Czeh Republic[4,27].

8. Calaverite $AuTe_2$ – Monoclinic System; Sulfide (Telluride) Class; (Mwt = 452.17 g/mol; 56.44% Te and 43.56% Au); Type locality: Stanislaus Mine, Calaveras County, California, USA; named after its locality. Paragenesis: usually in veins of quartz of low-temperature; also in medium high-temperature deposits, associated with quartz, hessite, sylvanite, altaite, coloradoite, rickardite, arsenopyrite, tetrahedrite-tennantite, sphalerite, stibnite and fluorite. Principal occurrences: USA, Chile, Mexico, Canada, Russia, Japão, Australia, Fiji Islands and Phillipines[4,27].

9. Criddleite $TlAg_2Au_3Sb_{10}S_{10}$ – Monoclinic System; Sulfosalt Class; (Mwt = 2,549.18 g/mol; 8.02% Tl, 8.46% Ag, 47.76% Sb, 23.18 % Au and 12.58% S); Type locality: Golden Giant Mine and Page-Williams Mine, Hemlo Gold Deposit, Marathon, Ontario, Canada; the name is a homage to the English mineralogist Alan Criddle (1944-2002). Paragenesis: occurs in hydrothermal ore veins associated with arsenopyrite, aurostibite, gold, quartz, stibiconite, pyrite and fluorapophyllite. Principal occurrences: Canada and France[4,28,29].

10. Fischesserite Ag_3AuSe_2 – Cubic System; Sulfide (Selenide) Class; (Mwt = 678.49 g/mol; 47.69% Ag, 29.03% Au and 23.28% Se); Type locality: Predborice, Czech Republic; the name is a homage to Raymond Fischesser, Director of the National School of Mines, Paris. Paragenesis: occurs in carbonate veins in epithermal metal deposits, associated with acanthite, aguilarite, gold, naumannite, marcasite, calcite and baryte. Principal occurrences: USA, Argentina, Chile, Czech Republic, Canada and England[4,30,55].

11. Gold (Native gold) Au – Cubic System; Native Elements (Metals) Class; Copper Group; (Mwt = 196.97 g/mol; 100% Au); Type locality: unknown. Paragenesis: occur in hydrothermal quartz veins and placers deposits, associated with isomertieite, rucklidgeite, bismuthinite, sphalerite, bornite, platinum, arsenopalladinite, petzite, silver (electrum variety) and quartz. Principal occurrences: USA, Russia, Brazil, Romania and Republic of South Africa[2,4,15,22,34].

12. Hunchunite Au_2Pb – Cubic System; Native Elements (Intermetallic Alloys) Class; (Mwt = 556.58 g/mol; 9.69% Ag, 37.23% Pb and 53.08% Au); Type locality: Sandogou placer gold deposits of the Hunchun River, Hunchun, Jilin Province, People's Republic of China; named after its locality. Paragenesis: occurs in alluvial placers and hydrothermal ore veins, associated with anyuiite, gold, lead, alunite, andradite, atacamite, delafossite, pyrite, quartz, ferronickelplatinum and cuprite. Principal occurrences: People's Republic of China and Russia[4,32].

13. Kostovite $CuAuTe_4$ – Orthorhombic System; Sulfide (Telluride) Class; (Mwt = 770.91 g/mol; 8.24% Cu, 66.21% Te and 25.55% Au); Type locality: Chelopech, Bulgaria; the named is a homage to Bulgarian mineralogist Ivan Kostov. Paragenesis: occurs in gold and platinum-bearing replacement copper deposits, associated with gold, enargite, nagyagite, quartz, galena, petzite, hessite, pyrite, bornite, siderite, chalcopyrite and treasurite. Principal occurrences: Finland, Greece, Bulgaria, Mexico, USA and Uzbekistan[4,33].

14. Krennerite $(Au,Ag)Te_2$ – Orthorhombic System; Sulfide (Telluride) Class; (Mwt = 452.17 g/mol; 56.44% Te and 43.56% Au); Type locality: Săcărâmb, Hunedoara County, Metaliferi Mountains, Romania; the name is a homage to Hungarian mineralogist Joseph Krenner (1839-1920). Paragenesis: occurs in hydrothermal ore veins, associated with calaverite, colorodaite, gold, hessite, nagyagite, pyrite, sphalerite, sylvanite and quartz. Principal occurrences: Romania, Fiji Islands, Argentina, Australia, Finland, Canada, Hungary Japan, Mexico, Russia, Republic of South Africa and USA[4,35].

15. Maldonite Au_2Bi – Cubic System; Sulfide (Bismutite) Class; (Mwt = 602.91 g/mol; 34.66% Bi and 65.34% Au); Type locality: Maldon, Victoria, Australia; named after its locality. Paragenesis: found in gold-quartz vein of high temperature, intergrowth with gold and bismuth, associated with arsenopyrite, chalcopyrite, ferberite, galena, gold, sphalerite, pyrite and molybdenite. Principal occurrences: Australia, USA,

Canada, Republic of South Africa, Czech Republic, Finland, Romania, Russia, France, Greece, Japan, Marocco and Namibia[4,36].

16. Montbrayite $(Au,Sb)_2Te_3$ – Triclinic System; Sulfide (Telluride) Class; (Mwt = 739.12 g/mol; 8.24% Sb, 51.79% Te and 39.97% Au); Type locality: Robb-Montbray mine; Montbray Township, Québec, Canada; named after its locality. Paragenesis: coarsely crystalline masses, also found rimming gold grains, associated with altaite, calaverite, chalcopyrite, coloradoite, krennerite, melonite, petzite, quartz, ruckliedgeite, tellurobismuthinite and tetradymite. Principal occurrences: Australia, Canada, Finland, Mexico, Sweden and USA[4,37,38].

17. Museumite $Pb_5AuSbTe_2S_{12}$ – Monoclinic System; Sulfide Class; (Mwt = ? g/mol; 52.00% Pb, 10.68% Au, 6.16% Sb, 11.71% Te and 19.43% S); Type locality: Sãcãrâmb, Hunedoara County, Metaliferi Mountains, Romania; name is a homage to the museums of the world that preserve old samples. Paragenesis: mineral found in gold-telluride epithermal deposits of andesitic rocks, associated with nagyagite, calcite, coloradoite, hessite, petzite, quartz, sylvanite and rhodochrosite[6,32,33].

18. Muthmannite (Ag,Au)Te – Monoclinic System (?); Sulfide (Telluride) Class; (Mwt = 556.88 g/mol; 19.18% Ag, 46.51% Te and 34.31% Au); Type locality: Sãcãrâmb, Hunedoara County, Metaliferi Mountains, Romania. The name is a homage to German chemist Friedrich Muthmann (1861-1913). Paragenesis: occurs in intergrowths with krennerite, in epithermal hydrothermal veins, associated with nagyagite, tellurium, sylvanite, calcite, quartz and pyrite. Principal occurrences: Romania[4,41].

19. Nagyágite $(Te,Au)Pb(Pb,Sb)S_2$ – Monoclinic System; Sulfosalt Class; (Mwt = 1,059.12 g/mol; 4.93% Bi, 8.62% Sb, 30.12% Te, 19.56% Pb, 18.60% Au and 18.17% S); Type locality: Sãcãrâmb/Nagyág, Hunedoara County, Metaliferi Mountains, Romania; named after its locality. Paragenesis: occurs in epithermal hydrothermal veins, associated with calcite, krennerite, stutzite, muthmannite, alabandite, gold and petzite, and intergrowths with buckhornite in a quartz gangue containing tellurobismuthite, altaite, galena, calaverite and native gold. Principal occurrences: Romania, Argentina, USA, Armenia, Austria, Bulgaria, Canada, Czech Republic, Fiji Islands, Japan, Mexico, New Zealand and United Kingdom (Wales)[4,42,43].

20. Novodneprite $(AuPb_3)$ – Tetragonal System; intermetallic alloy; Type locality: Novodneprovskoe deposit, Northern Kazakhstan; named after its locality; Paragenesis: occurs in gold-arsenic-polimetallic deposit, associated with auricupride, bogdanovite, hunchunite, anyuiite, sorosite and yuanjiangite. Principal occurrence: Kazakhstan[7,15].

21. Penzhinite $(Ag,Cu)_4Au(S,Se)_4$ – Hexagonal System; Sulfide Class; (Mwt = 759.28 g/mol; 8.37% Cu, 42.62% Ag, 25.94% Au, 10.40% Se and 12.67% S)); Type locality: Sergeevskoe Au-Ag deposit, Penzhina River Basin, Kamchaktka Peninsula and Chukotka, Russia; named after its locality. Paragenesis: near surface Au-Ag deposit

in intergrowths with chalcopyrite, associated with aguilarite, galena and gold. Principal occurrences: Russia[4,37,44].

22. Petrovskaite AuAg(S,Se) – Monoclinic System; Sulfide Class; (Mwt = 339.25 g/mol; 31.80% Ag, 58.06% Au, 1.16% Se and 8.98% S); Type locality: Maikan ¨S¨ deposit, Pavlodar Region, Kazakhstan; the name is a homage to Russian mineralogist Nina Petrovskaia. Paragenesis: occurs like microscopic rims grains in gold deposits, associated with chlorargyrite. Principal occurrences: Kazakshtan and USA[4,45,46].

23. Petzite Ag_3AuTe_2 – Cubic System; Sulfide (Telluride) Class; (775.77 g/mol; 41.71% Ag, 32.90% Te, and 25.39% Au); Type locality: Săcărâmb, Hunedoara County, Metaliferi Mountains, Romania; the name is a homage to chemist W. Petz who discovered the mineral in 1845. Paragenesis: occurs in hydrothermal ore veins of gold deposits, associated with native gold, hessite, sylvanite, krennerite, calaverite, altaite, montbrayite, melonite, frohbergite, tetradymite, rickardite, vulcanite, pyrite and quartz. Principal occurrences: Romania, USA, Australia, Uzbekistan, Russia, Kazakhstan, Canada, Chile, Fiji Islands and Phillipines[4,47].

24. Sylvanite $AuAgTe_4$ – Monoclinic System; Sulfide (Telluride) Class; (Mwt = 429.89 g/mol; 6.27% Ag, 59.36% Te and 34.36 Au); Type locality: Baia de Aries/Offenbanya, Metaliferi Mountains, Transylvania, Romania; named after the Province of Transylvania (Romania), place where the mineral was firstly found. Paragenesis: occurs in hydrothermal ore veins of low temperature, associated with petzite, native gold, fluorite, rhodochrosite, pyrite, acanthite, nagyagite, calaverite, krennerite and quartz. Principal occurrences: Romania, USA, Canada, Australia and Fiji Islands[4,41].

25. Tetra-auricupride AuCu – Tetragonal System; Native Elements (Intermetallic Alloys) Class; (Mwt = 260.51 g/mol; 24.39% Cu and 75.61% Au); Type locality: Sardala (Saar-Dala), Qingshui River, Malas (Marneshi) County, Xingjiang Autonomous Region, People's Republic of China. Tetraferroplatinum group; named after its crystallographie and Au-Cu contents. Paragenesis: occurs in mafic and ultramafic serpentinites containing platinoids, associated with Principal occurrences: People's Republic of China, Russia, France, Republic of South Africa and Switzerland[4,48].

26. Uytenbogaardite Ag_3AuS_2 – Tetragonal System; Sulfide Class; (Mwt = 584.70 g/mol; 55.35% Ag, 33.69% Au and 10,97% Au); Type locality: Tambang Sawah, Benkoelen District, Sumatra, Indonesia; the name is a homage to Duch mineralogist Willem Uytenbogaardt. Paragenesis: occurs in hydrothermal Ag-Au veins, associated with galena, acanthite, native gold (variety electrum), chlorargyrite, naumannite and quartz. Principal occurrences: Indonesia, Russia, USA, Bolivia, Argentina and Slovak Republic[4,49,50].

27. Weishanite $(Au,Ag)_{1,2}Hg_{0,8}$ – Hexagonal System; Native Elements (Intermetallic Alloys) Class; (Mwt = 925.26 g/mol; 8.74% Ag, 43.36% Hg and 47.90% Au); Type locality: Poshan Mine District, Weishan, Tongbai, Henan Province, People's Republic

of China; named after its locality. Paragenesis: occurs in silicified zone of silver-rich part of an Au-Ag deposit in biotite-granulite, associated with raspite, biotite, xenotime-(Y), acanthite, native gold, native silver, sphalerite, galena, pyrite and pyrrhotite. Principal occurrences: People's Republic of China, Brazil (Sumidouro, Minas Gerais) and Slovak Republic[4,51,52].

28. Yuanjiangite AuSn – Tetragonal System; Native Elements (Intermetallic Alloys) Class; (Mwt = 315.68 g/mol; 37.60% Sn and 62.40% Au); Type locality: Yuanjiang River, Yuanlin, Hunan Province, People's Republic of China; named after its locality. Paragenesis: mineral found in alluvial placers, associated with cassiterite, cinnabar, diamond, native gold, native osmium, native platinum, pyrite, realgar, rutile and zircon. Principal occurrence: People's Republic of China[4,53].

29. Zvyagintsevite (Pd,Pt,Au)3(Pb,Sn) – Cubic System; Native Elements (Intermetallic Alloys Class); (Mwt = 531.12 g/mol; 5.59% Sn, 54.10% Pd, 7.35% Pt, 29.26% Pb and 3.71% Au); Zapolyarnyi and Taymyrskii mines, Noril'sk Ni-Cu camp, Taymyr (Dolgano-Nenets autonomous district, Polar Siberia, Russia; the name is a homage to Russian geochemistry Orest Evegnevich Zvyangintsev, who studied the platinum resourches of Russia. Paragenesis: occurs in diferentiated gabbro-diabases intrusives, associated with hessite, molybdenite, tarkianite and Ag-Au alloys. Principal occurrences: Russia, Canada, Finland, Denmark (Greenland) and USA[4,54].

CONCLUSIONS

The small number of gold minerals (29 species described and validated by IMA - International Mineralogical Association) is related to the low chemical reactivity and geochemical distribution of the chemical element in the Earth Crust. Only native gold, calaverite, krennerite, nagyagite, petzite and the sylvanite are industrial sources of the metal that also can be obtained as a subproduct of the copper, lead and zinc sulfides.

The majority of gold minerals are sulfides, tellurides and intermetallic alloy classes, originated by hydrothermal processes in ore veins.

The main gold producers on a global scale are: USA, Russia, Canada, and Republic of South Africa. The countries with major bulk reserves are: Brazil, Australia, People's Republic of China, and Russia. Brazil contains important auriferous deposits in Serra Pelada (Pará) and Alta Floresta (Pará and Mato Grosso States).

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$[Au\text{-}S_4]^Z$ AND $[Au\text{-}O_2S_2]^Z$ – TYPE COMPLEX COMPOUNDS RELATED BY ELECTRON-TRANSFER REACTIONS

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ABSTRACT

The syntheses and the properties of square-planar $[Au\text{-}S_4]^Z$ and $[Au\text{-}O_2S_2]^Z$ – type complex compounds, involved in electron-transfer reactions, are presented. The complexes obtained are characterized by elemental analysis, IR, visible, UV, ESR spectroscopy, conductivity and polarographic data.

KEYWORDS: Gold (III), complex compounds, electron-transfer reactions

RESUMO

A síntese e as propriedades dos compostos quadrado-planares $[Au\text{-}S_4]^Z$ e $[Au\text{-}O_2S_2]^Z$, envolvidos em reações de transferência de elétrons são apresentadas e discutidas. Os complexos obtidos foram caracterizados por análise elementar, espectroscopia infravermelha, visível, RES, condutividade e medidas polarográficas.

PALAVRAS CHAVE: Complexos de Au(III), reações de transferência de elétrons

INTRODUCTION

An increasing number of papers published in recent years deal with description of syntheses and properties of complex compounds formed by various metallic ions with bidentate heterocyclic ligands (S_2), (N, S) and (O, S)[1-10].

The special interest aroused by these complexes is due, among others, to the fact that the complex compounds, readily participate in electron-transfer reactions without modifying the coordination geometry[11, 12].

The data reported in this paper referring to $[M\text{-}S_4]^Z$ and $[M\text{-}O_2S_2]^Z$ – type will contribute to enrich the knowledge in this field, as they refer to complex compounds of Au (III) with 6-nitro-quinoxaline-2,3-dithiol (NQDT), 6,7-dinitro-quinoxaline-2,3-dithiol (DNQDT), 2,3-dithiobenzo-quinoxalene-5,10-dione (DTBQD), 5,6-dithiobenzo-7,8-phenazine (DTBP) and 2-hydroxy-3-mercaptomethyl-1,4-naphthoquinone (HMMNQ)[13].

EXPERIMENTAL PROCEDURE

Reagents: $H[AuCl_4]$ (Merch,p.a.) and ligands (NQDT, DNQDT, DTBQD, DTBP, HMMNQ), double recrystallized (alcoholic solutions).

Instruments: The IR spectra (KBr) were recorded on a Perkin-Elmer FT-1600 Hewlett Pachard instrument.

An Unicam UV-visible 2-300 spectrophotometer was used to perform the electronic spectra.

The ESR spectra were recorded with an IFA Bucharest AR 7-5 spectrometer, working in the X band (9060 MHz) and having a 100 kHz modulation of the magnetic field.

The spectra were obtained at room temperature with a Mn (II) standard ($g_3 = 2.03584$, $g_4 = 1.98040$, $H_4 = 3268.5$).

The polarograms were recorded with an Orion KTS 7-77-4/b instrument. The half-wave potentials of the solutions (10^{-3} M) of complexes were measured at room temperature, using a calomel reference electrod and a dropping mercury electrode; a 10^{-1} M solution of tetra-n-butylammonium perchlorate was used a supporting electrolyte. The electrical conductivity was determined on a Conductivity meter OK 102-1 Radelkis.

Preparation of complexes: The $[(C_2H_5)_4N]$ $[Au(NQDT)_2]$ was prepared according the following procedure: 1 g of metallic sodium was dissolved in 50 ml absolute methyl alcohol and 1,4 g of freshly prepared and purified NQDT was added to the solution under stirring, until complete dissolution.

To the solution this obtained, 0,5 g of $H[AuCl_4]$, was then added dropwise, during 18-20 minutes.

The solution was filtered, then the filtrate was treated with 1,5 g tetraethylammonium iodide, dissolved in a minimal amount of absolute mathanol.

The solution was allowed to stand for 5-6 hours.

Water was added until the first crystals appered. The product was filtered and dried under vacuum avernight.

All the other complexes have been prepared by a similar procedure.

RESULTS AND DISCUSSIONS

The complex compounds of Au (III) with the above-mentioned ligands are microcrystalline variously coloured substances, whose melting points are higher than that of the pure ligand (Table 1). They are stable in time, insoluble in the usual organic solvents and partially soluble in a hot mixture of methylene-cloride-absolute ethanol 1/1 (in volumes).

The results of the elemental analysis (Table 1), show that the complex compounds of Au (III) are of $R[AuL_2]$ – type, where $R = [(C_2H_5)_4N]^+$, L = NQDT, DNQDT, DTBQD, DTBP and $[AuL_2]Cl$ – type, where L = HMMNQ.

The formulations can be explained only if the dithiols act as bidentate ligands (S_2), participating in the formulation of complexes as dithiolate dianions, gold having +3 oxidation state. In the case of $[AuL_2]Cl$ – type complex, HMMNQ acts as bidentate monoanionic ligand (O, S).

Table 1. Analytical and physical data of complexes

Compound*	Colour	M.p. °C	Mol.** cond. $\Omega^{-1}cm^2mol^{-1}$	Analyses (%): Found/calcd.				
				Metal	C	S	N	H
$R[Au(NQDT)_2]$	yellow	169	94.5	24.30/ 24.59	36.71/ 35.95	15.98/ 15.33	12.98/ 12.23	3.84/ 3.51
$R[Au(DNQDT)_2]$	yellow-orange	173	96.3	21.12/ 21.96	32.94/ 32.11	14.88/ 14.27	7.47/ 7.80	2.83/ 2.90
$R[Au(DTBQD)_2]$	orange	138	95.8	22.24/ 22.62	44.72/ 44.09	8.65/ 8.04	14.33/ 14.70	3.05/ 3.21
$R[Au(DTBP)_2]$	deep-red	181	98.7	21.33/ 21.62	52.08/ 52.69	14.46/ 14.05	7.49/ 7.68	3.84/ 3.95
$[Au(HMMNQ)_2]Cl$	dark-red	147	94.9	29.15/ 29.38	39.86/ 39.37	9.92/ 9.55	—	2.31/ 2.09

*) R = $[(C_2H_5)_4N]^+$; **) 10^{-4}M DMF solution, 22°C

Table 2. Infrared spectra (cm^{-1})

Compound*)	υ_{S-H} valency υ_{O-H} valency	$\upsilon_{C=O}$	$\upsilon_{C=C}$ skeleton	υ_{NO2} asym.	υ_{NO2} sym.	υ_{C-N} $\upsilon_{C=N}$ valency	υ_{C-H} plane defor-mation	υ_{2CH} plane rocking	υ_{C-S} valency
NQDT	2450 m	-	1620 i	1560 m	1330 i	1270 i	1060 m	845 i	660 m
$R[Au(NQDT)_2]$	2100 w 2350 sh	-	1630 v.i.	1520 w	1320 sh	1210 sh	1010 v.i.	835 v.i.	665 w
DNQDT	2360 m	-	1610 i	1565 i	1340 m	1270 m	1045 m	855 m	655 m
$R[Au(DNQDT)_2]$	2350 sh	-	1616 i	1550 w	1360 w	1240 sh	1075 v.i.	850 sh	650 w
DTBQD	2450 m	1660 i	1335 m 1565 v.i	-	-	1270 v.i.	1050 m	810 u	650 m
$R [Au(DTBQD)_2]$	2350 sh	1650 i	-	-	-	1265 m	1040 w	835 m	645 w
DTBP	2350 m	1660 i	1355 v.i. 1585 m	-	-	1220 i 1245 v.i	1050 i	855 v.i	685 m
$R [Au(DTBP)_2]$	2328 sh	1660 i	1620 sh	-	-	1250 sh	1065 m	845 w	665sh
HMMNQ	3380 m	-	1545 i 1590 m	-	-	-.	1080 m	820 m	680 i
$R[Au(HMMNQ)_2]Cl$	-	-	1540 i 1580 m	-	-	-	1075 w	828 m	655 sh

*)R=$[(C_2H_5)_4N]^+$; v.i. = very intens; i = intense; m = medium; w = weak; sh = shoulder

In an attempt to obtain data on the nature of the chemical bond[14] in the complex compounds studied, we have recorded IR spectra both for pure ligands and for the corresponding complexes (Table 2).

The data presented in Table 2 show that the absorption bands due to vibrations of various groups, not involved in the coordination, appear in the infrared spectra of both free ligands and complex compounds in the same spectral domains, with unchanged or slighthy modified intensities. In the case of $[Au\text{-}S_4]^Z$ – type complexes (L = NQDT, DNQDT, DTBQD, DTBP) the characteristic bands of the S-H groups, which appear in the IR spectra of the free ligands as shoulders at 2450 cm^{-1}, 2360 cm^{-1} and 2350 cm^{-1}, are modified in shape in the spectra of complex compounds and are shifted, proving the involvement of such bands in the coordination process. It has also been found that, in the spectra of complex compounds the bands due to the vibration of C-S bonds are somewhat shifted and modifed, compared to the spectra of free ligands, and this is an additional evidence in favour of the coordination of dithiols by the S-H groups.

In the case of $[Au\text{-}O_2S_2]^Z$ – type complex, $[Au(HMMNQ)_2]^+$ respectively, the disappearance of the 3380 cm^{-1} vibration frequency of the O-H band can be noticed, proving the involvement of these group in the coordination. The characteristic band of S-H group, which appear in the spectra of the ligand as intense band at 680 cm^{-1}, in the complex spectrum appear at slightly modified frequencies, proving the involvement of these group in the coordination.

The geometry of the complex compounds obtained has been established by determining their visible and UV electronic spectra (Table 3).

Table 3. Electronic spectra in the UV and visible range

Compound	$1/\lambda$ (cm^{-1})	Assignment
$[(C_2H_5)_4N][Au(NQDT)_2]$	30840 37850 45420	$^1A_{1g} \rightarrow {}^1A_{2g}$ $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1B_{2u}$
$[(C_2H_5)_4N][Au(DNQDT)_2]$	31270 38440 45270	$^1A_{1g} \rightarrow {}^1A_{2g}$ $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1B_{2u}$
$[(C_2H_5)_4N][Au(DTBQD)_2]$	30980 37470 45290	$^1A_{1g} \rightarrow {}^1A_{2g}$ $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1B_{2u}$
$[(C_2H_5)_4N][Au(DTBP)_2]$	30780 36850	$^1A_{1g} \rightarrow {}^1A_{2g}$ $^1A_{1g} \rightarrow {}^1B_{1g}$
$[Au(HMMNQ)_2]Cl$	30330 37300 45420	$^1A_{1g} \rightarrow {}^1A_{2g}$ $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1B_{2u}$

The bands observed in the electronic spectra of the complexes studied were assigned according to Gray and Ballhausen[15] and Vanquickenborne[16]. They used to molecular orbital approach to explain the spectra of square-planar complexes of the d^8 elements: Ni (II), Pd (II), Pt (II) and Au (III).

The correspondence of these bands observed in the electronic spectra of Au (III) – complexes with those of $[Au(CN)_4]^-$ promts us to assume the following assignments:

$^1A_{1g} \rightarrow {}^1A_{2g}$ $[b_{2g}(\pi^*) \rightarrow b_{1g}(\sigma^*)]$, (d-d);
$^1A_{1g} \rightarrow {}^1B_{1g}$ $[b_{2g}(\pi^*) \rightarrow a_{1g}(\sigma^*)]$,(L → M charge transfer);
$^1A_{1g} \rightarrow {}^1B_{2u}$ $[b_{2g}(\pi^*) \rightarrow a_{2u}(\pi^*)]$, (d-d).

The correspondence of these bands observed in the prepared complexes, with the bands described for $[Au(CN)_4]^-$ leads to the conclusion that all these compounds have an analogous square-planar symmetry.

The study of the complex compounds has been completed with conductivity measurements (Table 1). These data show that the compounds investigated are electrolytes (1:1) with $\lambda = 94.5 - 98.7\ \Omega^{-1}cm^2mol^{-1}$, in 10^{-4}M DMF solutions, at 22°C. This data are close to the value of the electric conductivity of the known complex ion $[Au(TDT)_2]^-$, which is a 1:1 type electrolyte. These results are also in agreement with the oxidation state +3 of the gold, resulted from chemical analysis.

The complex compounds studied present no ESR signal, which agrees well with the supposed oxidation state +3 for gold.

The polarographic study (Table 4) of the complex combinations suggests the existence of the electron-transfer reactions, the following species can be obtained in this case:

$$[Au\text{-}S_4]^- \xrightleftharpoons[-e^-]{+e^-} [Au\text{-}S_4]^{2-}$$

$$[Au\text{-}O_2S_2]^+ \xrightleftharpoons[-e^-]{+e^-} [Au\text{-}O_2S_2]^0$$

Table 4. Polarographic data

Compound	$E_{1/2}$(V)	$E_{1/2}$(V)	$E_{1/2}$(V)
$[(C_2H_5)_4N][Au(NQDT)_2]$	-0.380	-0.610	-0.945
$[(C_2H_5)_4N][Au(DNQDT)_2]$	-0.392	-0.80	-
$[(C_2H_5)_4N][Au(DTBQD)_2]$	-0.378	-0.75	-0.95
$[(C_2H_5)_4N][Au(DTBP)_2]$	-0.384	-0.628	-
$[Au(HMMNQ)_2]Cl$	-0.284	-0.505	-

The other observed waves are due to the reduction of the ligands. The data collected in connection with these complexes show that, aside from participating in electron transfer reactions, the evidenced species can also be obtained chemically, because the half-wave potentials range between +0.95 V and –0.95 V, a region in which oxidizing or reducing agents do not break un the complex.

CONCLUSIONS

Five new complex compounds of Au (III) have been with heterocyclic ligands. Chemical analysis and the results of physico-chemical determination suggest that these compounds are of the $[Au\text{-}S_4]^-$ - type for NQDT, DNQDT, DTBQD, DTBP and $[Au\text{-}O_2S_2]^+$ - type for HMMNQ, and exhibit square-planar geometry. Polarography data prove their involvement in the electron-transfer processes.

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CHROMIUM (III) COMPLEXES ANIONS IN THE CHEMICAL ANALYSIS ANAFRANILE DETERMINATION

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ABSTRACT

Some new gravimetric, oxidimetric and spectrophotometric methods for the determination of anafranile as anafranile·$H[Cr(NCS)_4(amine)_2]$ have been described. Statistical treatment of the experimental data shows that the methods employed are sufficiently accurate and are not affected by systematic errors

KEYWORDS: Cr(III), anafranile determination, complex salts

RESUMO

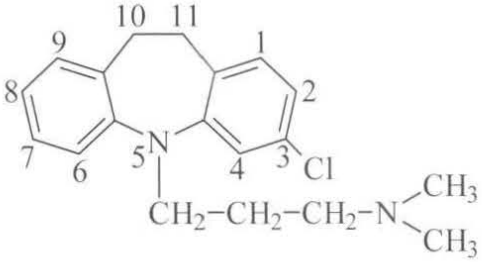
O presente trabalho descreve alguns métodos gravimétricos, espectrofotométricos e de oxidação novos para a determinação da afranila como afraniloH$[Cr\{NCS\}_4(amino)_2]$. Tratamento estatístico dos dados experimentais mostra que os métodos desenvolvidos tem precisão adequada e não são afetados por erros sistemáticos.

PALAVRAS CHAVE: Cromo(III), determinação de afranila,
sais complexos

INTRODUCTION

Anafranile (3-chlor-5-[3-(dimetilamine)-propil]-10,11-dihydro-5H-dibenzo [b,f] azepinehydrochlorate), chlomipramine hydrochlorate (3-chlorine-imipramide) is an antihistamine, anticholinergic, tricyclic antidepressive medicine. It is given in the form of tablets of 10, respectively 25mg anafranile hydrochlorate/tablet.

The structural formula of this drug is:



Anafranile is obtained through a similar method to that described for antideprin [1]. In the literature it does not mention many methods for determining this drug [2].

We have observed that in acid medium, anafranile precipitates quantitatively with Reinecke's salt and its analogous, of type $NH_4[Cr(NH_4)(amine)_2]$, where the amine is: aniline, toluidine, Et_2PhP, imidazole, cystamine etc., in the form of anafranile·$H[Cr(NH_4)(amine)_2]$. For this reason we could elaborate three methods for determining this drug by gravimetric, oxidimetric and spectrometric methods [3].

Anafranile compounds with Reinecke salt and its analogous are red-violet coloured, hardly soluble in water but easily soluble in acetone, DMF, DMSO, etc. The solutions obtained allowed us to make the spectrophotometric determination of this substance.

EXPERIMENTAL PROCEDURE

Synthesis of reagent $NH_4[Cr(NH_4)(amine)_2]$ was made according to the method of Ion Ganescu [4], starting with $K_3[Cr(NCS)_6]$ anhydrous and N-respective base.

The elementary analysis of anafranile complexes with complex anions of Cr(lll), type $[Cr(NCS)_4(amine)]$ was as follows:

- anafranile·$H[Cr(NH_4)(amine)_2]$
M=786.42
%Cr: calc. 6.61, found 6.57
%N: calc. 10.68, found 10.62
%S: calc. 16.31m found 16.26.
- anafranile·$H[Cr(NCS)_4(Et_2PhP)_2]$
M=880,57
%Cr: calc. 5.90, found 5.87
%N: calc. 9.54, found 9.74
%S: calc. 14.54, found 14.48.
- anafranile·$H[Cr(NCS)_4(pilocarpine)_2]$
M=880,57

%Cr: calc. 5.12, found 5.07
%N: calc. 11.02, found 10.98
%S: calc. 12.60, found 12.54.
- anafranile·H[Cr(NCS)$_4$(scopolamine)$_2$]
M=1199,88
%Cr: calc. 4.33, found 4.29
%N: calc. 9.33, found 9.28
%S: calc. 10.67, found 10.61.
- anafranile·H[Cr(NCS)$_4$(cystamine)$_2$]
M=880,56
%Cr: calc. 5.90, found 5.87
%N: calc. 22.26, found 22.15
%S: calc. 14.54, found 14.48.

RESULTS AND DISCUSSION

New complexes salts of anafranile with thiocyanatochromic complexes of type anafranile·H[Cr(NCS)$_4$(pilocarpine)$_2$]

A sample of 0.01-0.02 moles of anafranile was treated with distilled water up to 50-80mL, subsequently, a solution 3% of thiocyanatochromic complex salt was added until the above solution of the precipitate was red-violet. The reactions mixture was allowed to stay for 15-20 minutes and then was filtered, washed with distilled water and dried. The experimental results are presented in Table 1.

Table 1. New complex salts of type anafranile·H[Cr(NCS)$_4$(pilocarpine)$_2$].

Crt no.	Combination	Molecular Weight calculated	Yield %	Microcrystalline character	Analysis %	
					Calc.	Found
1	A·H[Cr(NCS)$_4$(NH$_3$)$_2$]	614.29	97	Red-violet Microcrystals	Cr:8.46 S:20.88 N:13.67	8.42 20.81 13.62
2	A·H[Cr(NCS)$_4$(aniline)$_2$]	786.42	98	”	Cr:6.61 S:16.31 N:10.68	6.57 15.69 10.26
3	A·H[Cr(NCS)$_4$(benzylamine)$_2$]	814.42	96	”	Cr:6.38 S:15.75 N:10.31	6.34 15.69 10.26
4	A·H[Cr(NCS)$_4$(imidazole)$_2$]	736.58	93	”	Cr:7.06 S:17.41 N:15.21	7.02 17.36 15.15
5	A·H[Cr(NCS)$_4$(benztriazole)$_2$]	839.46	95	”	Cr:6.19 S:15.28 N:16.68	6.16 15.22 16.61
6	A·H[Cr(NCS)$_4$(urotropine)$_2$]	880.56	96	”	Cr:5.90 S:14.54 N:22.26	5.87 14.48 22.15

A= anafranile; Cr as Cr_2O_3; N-gas-volumetric.

Gravimetric determination

A sample of 2.1-21 mg anafranile in the form of hydrochlorate was diluted with distilled water to a volume of 50 mL and then precipitated with reagent $NH_4[Cr(NCS)_4(amine)_2]$, where amine is aniline and Et_2PhP, in hydroalcoholic solution (2%). After 15-20 minutes, the precipitate was filtered by using a G4 filter crucible, washed two-three times with 10 mL distilled water until the filtrate flowed colorless, dried in a drying oven at 105-110°C for an hour and after that it was weighed with an analytical balance. [5,6] The experimental results are shown in Table 2.

Table 2. The gravimetric determination of anafranile after precipitation in the form of anafranile$\cdot H[Cr(NCS)_4(aniline)_2]$ (A) and anafranile$\cdot H[Cr(NCS)_4(Et_2PhP)_2]$ (B).

Anafranile mg taken	Form of determination							
	A				B			
	Weighed $G_{complex}$	Anafr. mg found	Error		Weighed $G_{complex}$	Anafr. mg found	Error	
			mg	%			mg	%
2.1	5.20	2.08	-0.02	0.95	5.85	2.09	-0.01	0.48
4.2	10.54	4.22	+0.02	0.48	11.81	4.22	+0.02	0.47
8.4	20.96	8.39	-0.01	0.12	23.57	8.43	+0.03	0.36
12.6	31.53	12.62	+0.02	0.16	35.12	12.56	-0.04	0.32
16.8	42.06	16.84	+0.04	0.24	47.07	16.83	+0.03	0.18
21.0	52.57	21.05	+0.05	0.24	58.87	21.05	+0.05	0.24
M_A=786.42; f_A=0.4004 $\overline{X}$=8.41 $S^2=6.33\cdot10^{-4}$ $S=2.51.10^{-2}$ t=0.4 $t_{n-1,\alpha}=2.26$; α=95% $\overline{X}-ts<A<\overline{X}+ts$ 8.39<8.40<8.41					M_A=880.57; f_B=0.3576 $\overline{X}$=16.81 $S^2=7.66\cdot10^{-4}$ $S=2.51.10^{-2}$ t=0.36 $t_{n-1,\alpha}=7.26$; α=95% $\overline{X}-ts<A<\overline{X}+ts$ 16.79<16.80<16.81			

Oxidimetric determination

A sample of 2.1-21 mg anafranile was treated with HCl as described above, then precipitated with thiocyanatochromic reagents; the precipitate was filtered with filter paper using a 5 diameter Büchner funnel and it was washed with 10 mL distilled water until the filtrate flowed colourless. The paper with the respective precipitate was transferred moved in a high- shaped Berzelius glass of 500 mL to which 20 mL solution of NaOH 5% are added. The glass containing the precipitate is boiled on a gas burner sieve when green-coloured $Cr(OH)_3$ appears. $Cr(OH)_3$ is destroyed with HCl so that its normal condition in each sample should be 1.7 N. Then 5 mL CCl_4 and

110 drops ICl [7] are added, it is titrated with a solution 0.1 N $KMnO_4$, $KBrO_3$ and KIO_3 under continuous stirring until the violet layer of CCl_4 discolors. The experimental results are shown in Table 3.

Table 3. Oxidimetric determination of anafranile after precipitation in the form of anafranile$\cdot$H[Cr(NCS)$_4$(pilocarpine)$_2$] (A) and anafranile$\cdot$H[Cr(NCS)$_4$(scopolamine)$_2$]. (B).

Anafr.mg taken	Det. no.	$\overline{X}$ mg	S	t_a	t_b	$t_{n-1,\alpha}$ α=95%
Permanganometric determination						
2.1	10	2.109	$2.81 \cdot 10^{-2}$	$6.978 \cdot 10^{-4}$	$18.46 \cdot 10^{-2}$	2.57
16.8	10	16.83	$2.77 \cdot 10^{-2}$	$6.978 \cdot 10^{-4}$	$14.46 \cdot 10^{-2}$	2.57
Bromatometric determination						
4.2	10	4.211	$2.52 \cdot 10^{-2}$	$28.69 \cdot 10^{-4}$	$18.51 \cdot 10^{-2}$	2.57
12.6	10	12.613	$2.77 \cdot 10^{-2}$	$23.11 \cdot 10^{-4}$	$18.36 \cdot 10^{-2}$	2.57
Iodatometric determination						
8.4	10	8.411	$2.51 \cdot 10^{-2}$	$26.06 \cdot 10^{-4}$	$18.03 \cdot 10^{-2}$	2.57
21.0	10	21.011	$2.52 \cdot 10^{-2}$	$22.89 \cdot 10^{-4}$	$18.45 \cdot 10^{-2}$	2.57

1 mL solution 0.1N ($KMnO_4$, $KBrO_3$, KIO_3) is equivalent to 1.312 mg anafranile.

This method is very responsive because 1 mole of SCN^- consumes six equivalents of oxidizer:

$$SCN^- - 6e^- + 4H_2O \rightarrow SO_4^{2-} + HCN + 7H^+$$
$$5SCN^- + 6MnO_4^- + 13H^+ \rightarrow 6Mn^{2+} + 5SO_4^{2-} + 5HCN + 4H_2O$$
$$2SCN^- + 3IO_3^- + 4H^+ \rightarrow 2SO_4^{2-} + 3I^+ + 2HCN + H_2O$$
$$2SCN- + 3BrO_3^- + 4H^+ \rightarrow 2SO_4^{2-} + 3Br^+ + 2HCN + H_2O$$

The method is accurate, rapid and, according to statistical data, it is not affected by systematic errors.

Spectrophotometric determination

A sample of 2.15-2.17 mg anafranile in the form of hydrochloride are precipitated with reagent NH_4[Cr(NCS)$_4$(cystamine)$_2$] in hydroalcoholic solution 2%. The precipitates was filtered with a G_4 crucible, it was washed two-three times with 10 mL distilled water until the filtrate flowed colourless and then it was dissolved in acetone. The red-violet solution is moved to a volumetric flask balloon and was completed with acetone up to the mark. The absorbance of this solution was measured at 540 nm. [9,10] The experimental results are shown in Table 4.

$$y-\bar{y}=r\frac{\sigma_x}{\sigma_y}(x-\bar{x})\text{; }y=0.0605049x+0.000674$$

$$x-\bar{x}=r\frac{\sigma_x}{\sigma_y}(y-\bar{y})\text{; }x=16.4925664y+0.0093486$$

The concentration domain, where the Lambert-Beer law is followed, lies between 0.086 mg and 0.6868 mg anafranile.

The molar extinction coefficient is ε=1333.4048 Lcm^{-1}mole^{-1}. The calibration curve for spectrophotometric determination of anafranile in the form of anafranile·H[Cr(NCS)$_4$(cystamine)$_2$] is presented in figure 1.

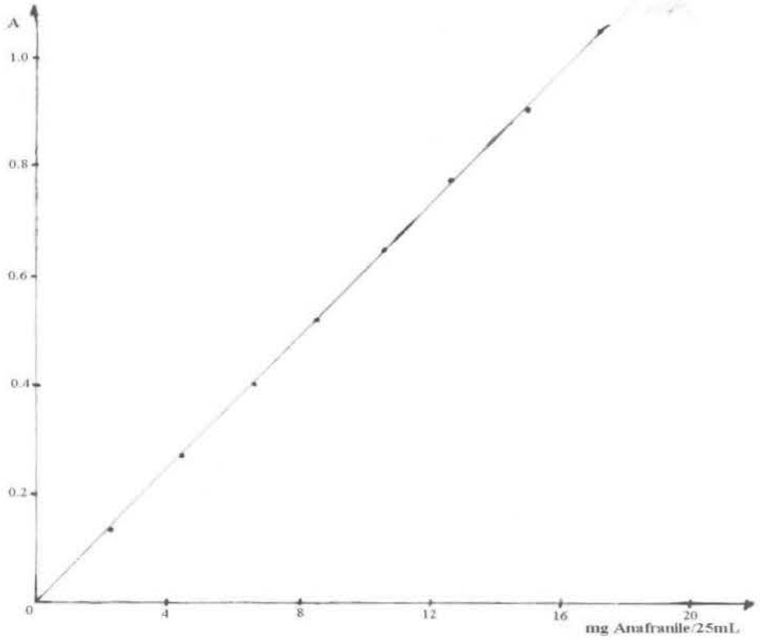


Figure 1. Determination of anafranile in the form of anafranile·H[Cr(NCS)$_4$(cystamine)$_2$].

The variation of absorbance with wave length is presented in Figure 2 and the variation of colour depending with time is presented in Figure 3.

Table 4. Spectrophotometric determination of anafranile, after precipitation, in the form of anafranile·$H[Cr(NCS)_4(cystamine)_2]$.

Crt. no.	x mg	x^2	y	y^2	xy	x+y	$(x+y)^2$
1	2.15	4.6225	0.13	0.0169	0.2795	2.28	5.1984
2	4.29	18.4041	0.26	0.0676	1.1154	4.55	20.7025
3	6.44	41.4736	0.39	0.1521	2.5116	6.83	46.6489
4	8.59	73.6164	0.52	0.2704	4.4616	9.10	82.8100
5	10.73	115.1329	0.65	0.4225	6.9745	11.38	129.5044
6	12.88	165.8944	0.78	0.6084	10.0464	13.66	186.5956
7	15.02	225.6004	0.91	0.8281	13.6682	15.93	253.7649
8	17.17	294.8089	1.04	1.0816	17.8568	18.21	331.6041
Total	77.26	939.5532	4.68	3.4476	56.914	81.94	1056.8288

From these data statistically processed [8,11], we verified the calculations as follows:

$\Sigma x^2 + \Sigma y^2 + 2\Sigma xy = 1056.8288$

$\Sigma (x+y)^2 = 1056.8288$

We can notice that the two values are equal. This means that the method is reproducible and precise.

The standard deviations and the regression coefficient were calculated as follow:

$$\sigma_x = \sqrt{\frac{\sum x^2}{n} - \bar{x}^2} = 4.92; \ \bar{x} = 9.6575$$

$$\sigma_y = \sqrt{\frac{\sum y^2}{n} - \bar{y}^2} = 0.298; \ \bar{y} = 0.585$$

$$r = \frac{\frac{\sum xy}{n} - \bar{x}\bar{y}}{\sigma_x \sigma_y} = 0.99894 \approx 1$$

The value of r≈1 shows that the results obtained with this method are reproducible and the error is negligible.

The equations show the dependence between absorbance and concentration of active product in the sample (mg), deducted by linear regression method are:

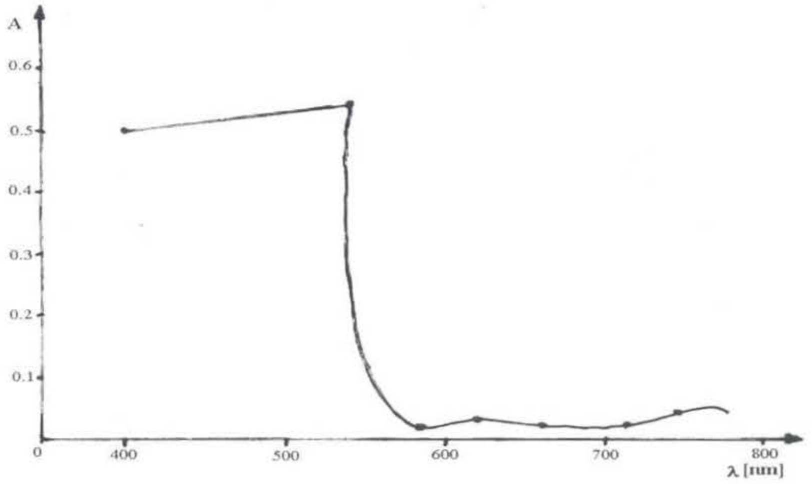


Figure 2. Variation of absorbance of anafranile complex with wave lenth.

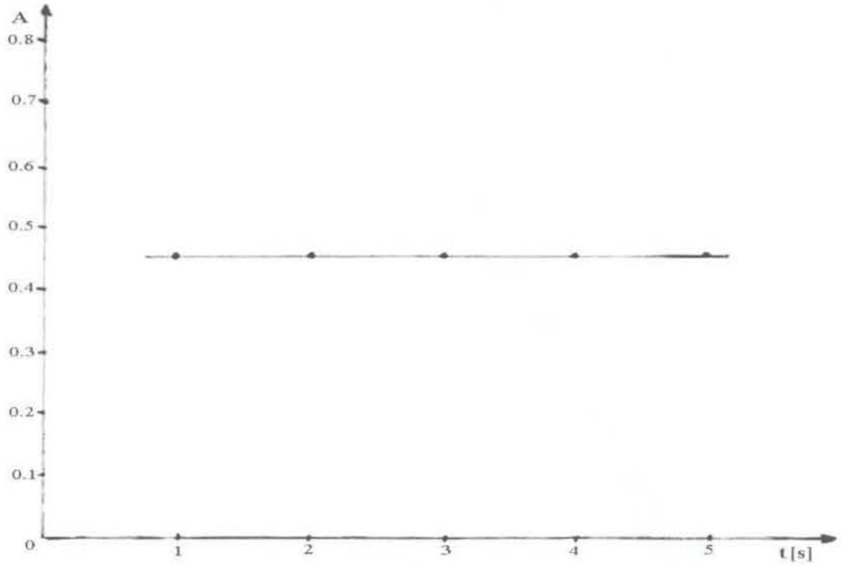


Figure 3. Variation of colour with depending on time.

Determination of anafranile in tablets

Twenty tablets of anafranile containing 10 mg anafranile hydrochlorate/tablet were pulverized in a mortar. From the resulting powder, well homogenized, 0.10-

0.15g were weighed on the analytical balance and were treated as mentioned above. The precipitate, washed, in order to remove the excess reagent, was transferred quantitatively to a 100 mL flask by using acetone and is completed under the same conditions described for the standard curve (λ=540nm). The quantity of anafranile in each sample was determined with the help of the standardization curve presented in Figure 1.

CONCLUSIONS

Anafranile can be determined quantitatively in the form of thiocyanatochromic complexes, gravimetrically, oxidimetrically and spectrophotometrically.

Every experimental result was statistically processed. The results showed that the methods developed were not influenced by systematic errors, were quite rapid and accurate. We recommended these methods to all laboratories for analysis and control of drugs.

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INVESTIGATION OF CARBON STEEL CORROSION IN DILUTED AMMONIACAL MEDIA

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ABSTRACT

Electrochemical measurements (steady-state current-voltage curves) were coupled with Mössbauer spectroscopy techniques to investigate the corrosion of carbon steel in diluted ammoniacal media. The corrosion current for carbon steel in diluted ammoniacal media was determined from galvanostatic measurements, through extrapolation of the Tafel segments at the corrosion potential. Mössbauer measurements were performed at room temperature in the transmission (TMS) and conversion electron spectroscopy (CEMS) using a conventional constant-accelerating spectrometer with a ^{57}Co-Rh source. The result of the corrosion is the layer appearance (nonstoichiometric iron oxide) on the sample surface.

KEYWORDS: ammoniacal media; carbon steel, corrosion, Mössbauer spectroscopy

RESUMO

A corrosão do aço de carbono em meio amoniacal diluído foi estudada usando técnicas de espectroscopia Mössbauer acoplada com medidas eletroquímicas (curvas potencial-corrente).A corrente de corrosão do aço carbono em meio amoniacal diluído foi determinada com medidas galvanoestáticas , extrapolando os segmentos de Tafel no potencial de corrosão. As medidas Mössbauer foram efetuadas à temperatura ambiente com espectroscopia eletrônica de transmissão e conversão (EMT e EMCE) usando um espectrômetro convencional com aceleração constante e uma fonte de ^{57}Co-Rh. O resultado da corrosão é o aparecimento de uma camada (óxido de ferro não-estequiométrico) na superfície da amostra.

PALAVRAS CHAVE: ***aço de carbono, meio amoniacal, corrosão, espectroscopia Mössbauer***

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INTRODUCTION

Industrial and residual waters containing ammonia/ammonium have been long neglected by researchers, as these were considered inoffensive to the environment and regarding the corrosion they exercise on the pipes used in cooling circuits especially in the ammonium-based fertilizers industry.

Recent research has demonstrated that waters containing ammonia/ammonium have negative actions on the environment concerning over-fertilization of surface waters resulting in the multiplication of the inferior organisms, e.g. phytoplankton and algae, in the toxic action on the live organisms in waters and in the destruction of oxygen through nitrification.[1,2]

The corrosion action of the ammoniacal solutions is associated with the nitrification of the ammonium in tow stages: first as a nitrite and then as a nitrate. The first stage is achieved by the *Nitrosomonas* bacteria that oxydate the ammonium ion. At the second stage, the nitrite is turned into nitrate in presence of *Nitrobacter* bacteria.

The first stage is very slow, but the second is relatively fast. This is why only residual concentrations of nitrite can be found. There have been many studies on the ammonium recovery from water through chemical procedures[3,4] or through biological purification.[5,6] The processes of corrosion or of inhibition can be studied by associating electrochemical measurements with analytical tehniques.[7]

The aim of the present study is to investigate the carbon steel corrosion in diluted ammoniacal media by using electrochemical measurements.

In the carbon steel fabrication, no significant differences appear in the composition of different ingots, and this is why the corrosion rates do not differ under the same given conditions.

The variation in the ratio proportion of carbon manganese and silicon (elements that condition the value of the mechanic characteristics) does not influence the sensitivity to the corrosive action too much. Nevertheless, an increase in the ratio of these elements leads to some decrease in the sensitivity to the corrosive action, which is not the case with carbon steel. In the corrosion processes, the common carbon steels liberate a very small quantity of hydrogen. In the representative corrosion processes water appears as a solubilization agent, as a reactant and as favoring the ionic conductivity of the surface layer, a conductibility necessary to the transfer of ferrous ions.[8,9]

The basic/alkaline media determine the start of punctiform corrosion process and its development in the classic way of the electrochemical corrosion.

Experimental details

The samples chosen for this investigation was carbon steel with the following composition: C = 0.35%, Mn = 0.65%, Si = 0.25%, S = 0.035% and the remainder iron up to 100%. For all experiments the samples were polished, cleaned in water, degreased in ethilic alcohol and dried in warm air.

The corrosion medium was produced from ammoniacal solutions that contained: 10^{-3} N NH_3 and different concentrations of NH_4Cl and NH_4NO_3. The investigation has been done at a temperature of 25°C, while the corrosive medium has been kept in contact with air.

Electrochemical measurements

A standard corrosion cell was used to study polarization. The working electrode was a carbon steel plate with an area of 4 cm^2. A calomel-saturated electrode was used as a reference electrode and the auxiliary electrode was a carbon steel plate identical to that of the working electrode. The galvanostatic measurements were made by using a continuos current supply in the circuit, a variable resistance, a miliampermetre and a milivoltmetre. Data were computerized.

RESULTS AND DISCUSSION

We have studied the corrosion process of the carbon steel in diluted ammoniacal solutions, which contain dissolved ammonia and different concentrations of ammonium chloride and ammonium nitrate.

The study of the carbon steel corrosion in diluted ammoniacal waters containing Cl^- anion

The anodic polarization curves in stationary conditions for the carbon steel sample in ammoniacal solutions containing 10^{-3} N NH_3 and different concentrations of NH_4Cl are presented in figure 1.

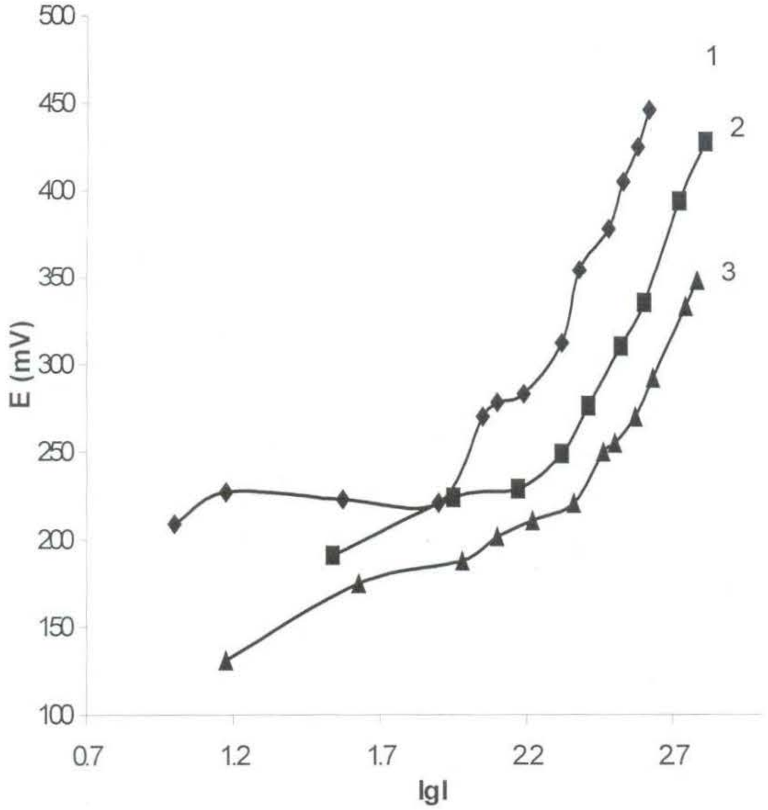

Figure 1. The anodic polarization curves for carbon steel in ammoniacal solutions containing different concentrations of NH_4Cl, such as: (1) 10^{-3} M; (2) 3 x 10^{-3} M; (3) 5 x 10^{-3} M.

It can be observed that while the concentration of NH_4Cl increases, the anodic over-voltage decreases. Steel is active and dissolves after a Tafel-type slope b_a at 41±6 mV.

The cathodic polarization curves are presented in figure 2. The supplementary cathodic polarization leads to an increase in the linear segments from 33.3 mV to 43.3 mV for a NH_4Cl concentration of 10^{-3} M. Also an increase in the NH_4Cl concentration is concurrent with the increase in the cathodic over-voltage (figure 2).

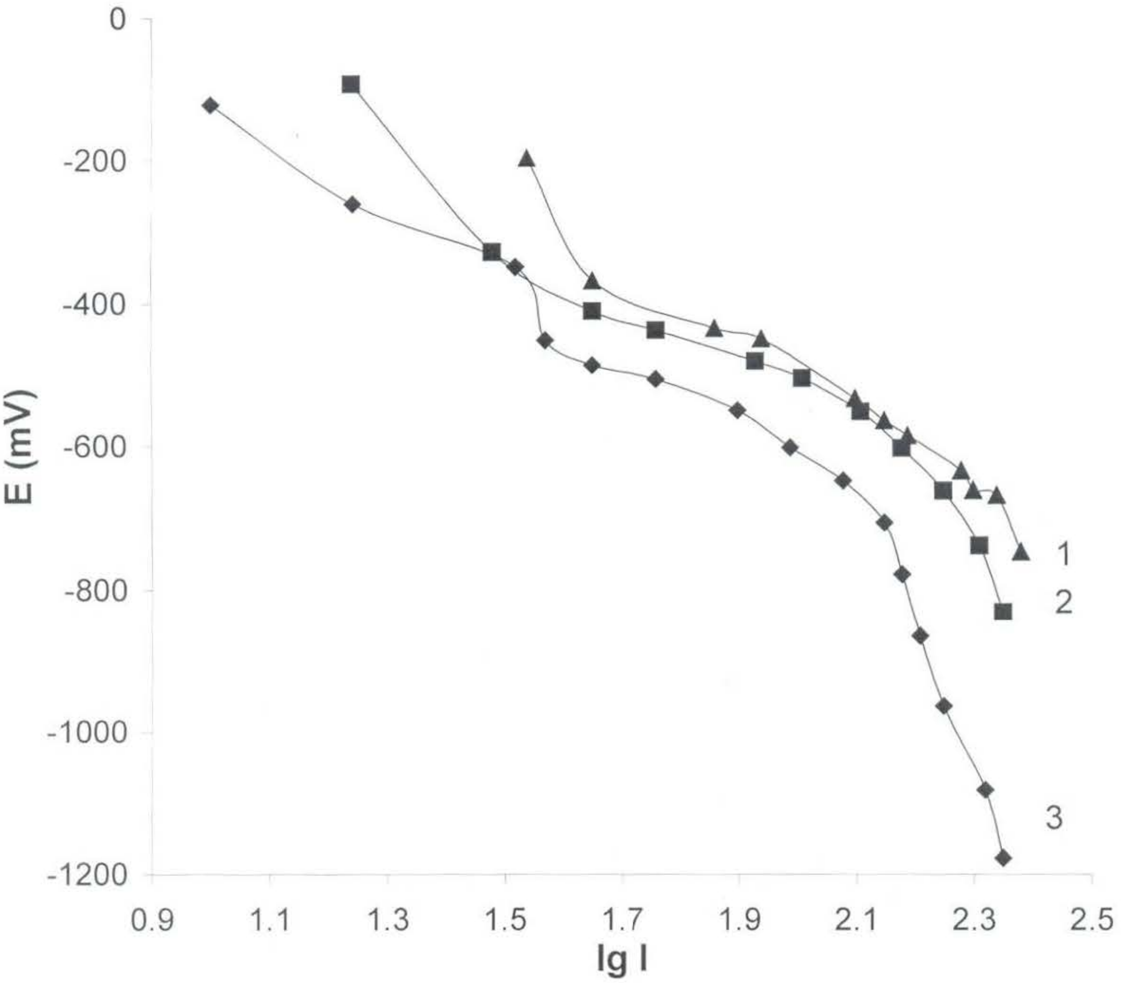

Figure 2. The cathodic polarization curves for carbon steel in ammoniacal solutions containing different concentrations of NH_4Cl such as: (1) 10^{-3} M; (2) 3×10^{-3} M; (3) 5×10^{-3} M.

The presence of Cl^- anion in the ammoniacal solution slightly decreases the pH value, while no spontaneous passivation of the metal surface can be observed. The polarization curve E = f(I) in figure 3 proves that steel is active in the current density field under study, between 15 mA/dm^2 and 800 mA/dm^2.

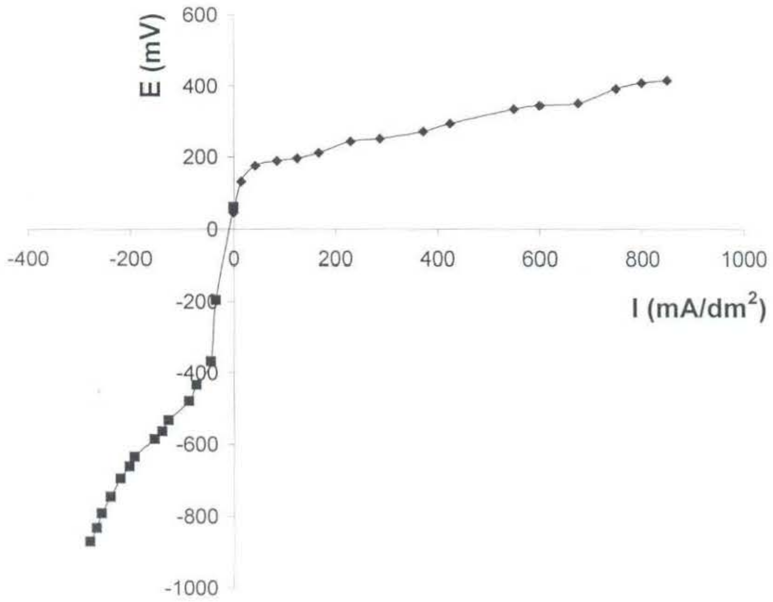

Figure 3. The polarization curve of carbon steel in the solution containing 10^{-3} N NH_3 and 5×10^{-3} M NH_4Cl.

For the determination of the corrosion current the anodic and cathodic polarization curves have been drawn for a sample of carbon steel in ammoniacal solution containing 10^{-3} N NH_3 and 10^{-3} M NH_4Cl for potentials far apart from the corrosion potential (figure 4).

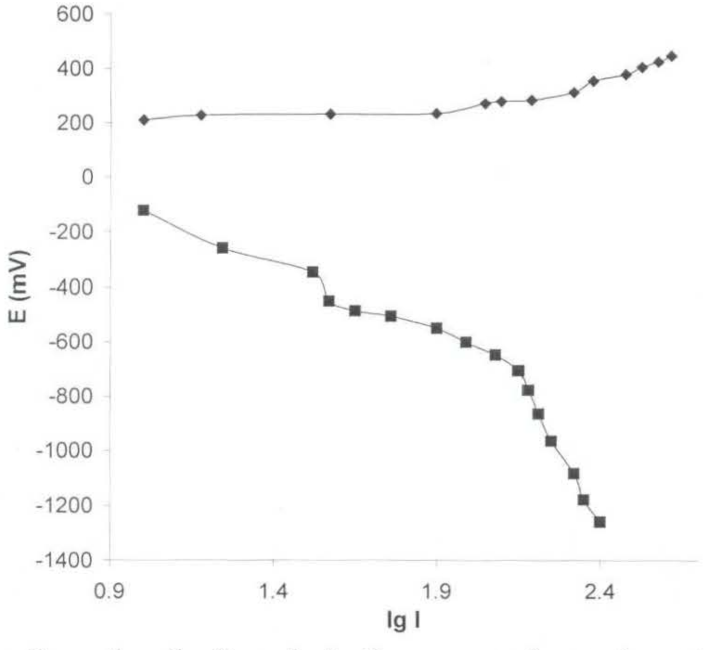

Figure 4. The anodic and cathodic polarization curves for carbon steel in ammoniacal solution containing 10^{-3} N NH_3 and 10^{-3} M NH_4Cl.

By extrapolation of the linear segments at y = 0 the corrosion current has been determined. The results are presented in Table 1.

Table 1. The corrosion current for carbon steel in ammoniacal solution containing 10^{-3} N NH_3 and 10^{-3} M NH_4Cl.

	From anodic	From cathodic	From anodic + cathodic
I_{cor} (mA/dm^2)	8.87	3.32	4.31

The corrosion currents resulting from extrapolation of Tafel segments on the last part of the curves for different NH_4Cl concentration are presented in Table 2.

Table 2. The electrochemical parameters of the carbon steel sample in solution containing 10^{-3} N NH_3 and different NH_4Cl concentrations.

Conc. NH_4Cl (mol/L)	10^{-4}	10^{-3}	3×10^{-3}	5×10^{-3}
E_{cor} (mV)	126	90	37	33
I_{cor}anodic (mA/dm^2)	1.7	12.8	33	47
I_{cor}cathodic (mA/dm^2)	6.5	17	50	59
I_{cor}anodic + cathodic (mA/dm^2)	5	13	47	57

For the solution containing 10^{-3} M NH_4Cl at current densities higher than 100 mA/dm^2, it can be observed an increase of the corrosion current from 4.3 mA/dm^2 to 13 mA/dm^2, which shows that while the current densities increase, the electrode surface changes, the metal dissolves. Also compounds are formed such as $Fe(OH)_3$, which precipitate in the solution and from non-adherent, porous and non-uniform layers on the metal surface, under which the corrosion process continues.

The cathodic reduction of the solvent requires a higher over-voltage for decreasing NH_4Cl concentrations. The cathodic process is also determined by the total transfer of all compounds reduced cathodically (O_2, $NH_4^+$and H_3O^+)

The study of the carbon steel corrosion in diluted ammoniacal waters containing NO_3^- anion

The anodic and cathodic polarization curves are presented in figure 5. The corrosion process is spontaneous, while the NO_3^- anion has hardly any influence on the solution pH. If experimentally the conditions created for the achievement of corrosion can differ from the real corrosion conditions, the dissolving of steel was inhibited by the presence of NO_3^- anions. The solution pH at the level of the corrosive spot increases with the NH_4Cl solution, leading to a slow down in the rate of dissolution. The development of the corrosive spot is evidently inhibited by NO_3^- anion or is a combined effect resulting from the synergetic action of the ammonium with NO_3^-.

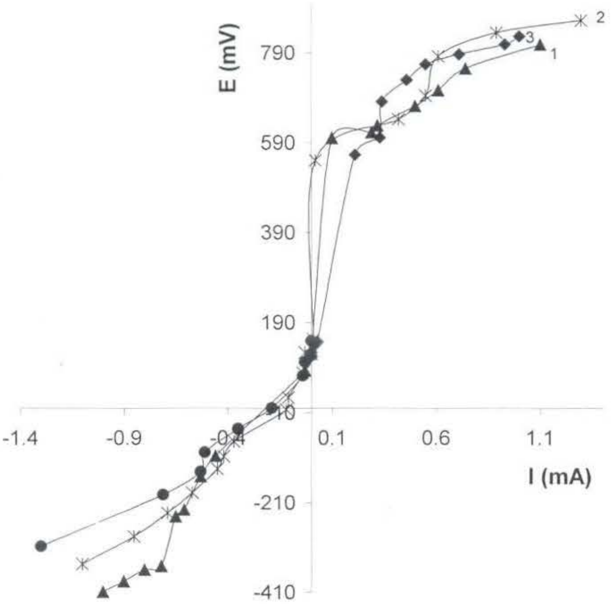

Figure 5 The polarization curves for carbon steel in 10^{-3} N ammoniacal solution containing different NH_4NO_3 concentrations: (1) 10^{-3} M; (2) 3 x 10^{-3} M; (3) 5 x 10^{-3} M.

At low current densities the curve presents a significant leap from the corrosion potential to a potential of 600 mV, after which the process proceeds slowly (figure 6), with metal dissolving after a Tafel-type curve b_a at 43±10 mV.

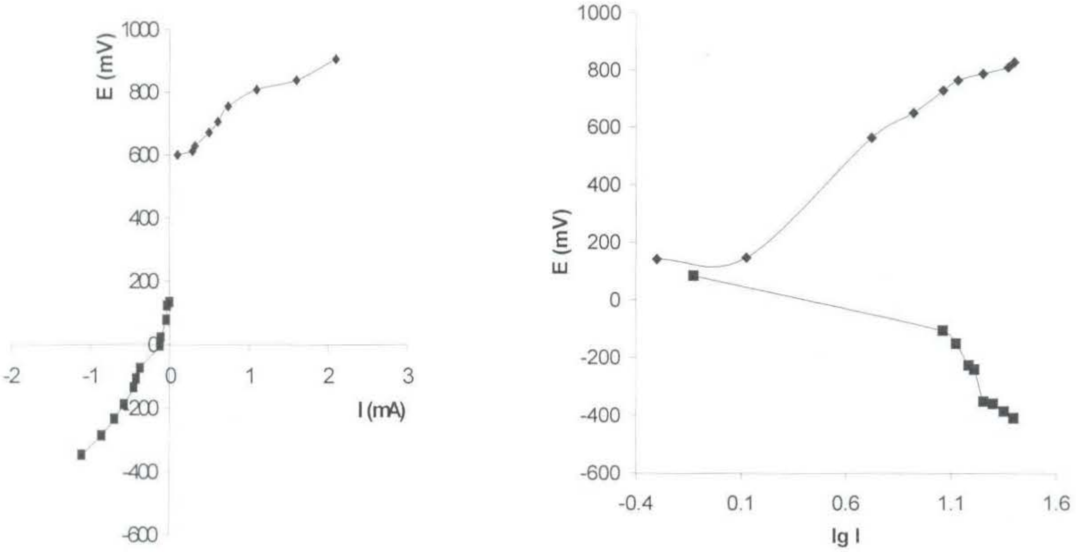

Figure 6. The polarization curves for carbon steel in ammoniacal solution containing 10^{-3} N NH_3 and 3 x 10^{-3} M NH_4NO_3.

The cathodic process proceeds with depolarization of NH_4^+, O_2 and of the solvent at cathodic over-voltages increases concurrent with the increases in NO_3^- concentration.

The corrosion currents were determined from the anodic and cathodic Tafel segments for the final portions of the polarization curves. Data are presented in Table 3.

Table 3. The electrochemical parameters for the carbon steel sample in ammoniacal solution 10^{-3} N NH_3 and different NH_4NO_3 concentrations.

Conc. NH_4NO_3 (mol/L)	10^{-3}	3×10^{-3}	5×10^{-3}
E_{cor} (mV)	138	128	132
I_{cor}anodic (mA/dm^2)	0.09	0.31	0.75
I_{cor}cathodic (mA/dm^2)	5.8	3.79	5.7
I_{cor}anodic + cathodic (mA/dm^2)	2.03	1.46	2.65

Irrespective of the NO_3^- concentration, the corrosion currents have very close values, which confirms the passivant role of the anion at current densities higher than 2 mA/dm^2. The corrosion currents are significantly smaller than in solutions containing NH_4Cl and have higher values than in solutions containing only dissolved ammonium.

Mössbauer spectroscopy was performed at room temperature in the transsmision (TMS) and conversion electron spectroscopy (CEMS) using a constant accelerating spectrometer with a ^{57}Co-Rh source.

In figures 7 and 8 are presented the TMS and CEMS spectra of reference sample before corrosion processes. The best fitting of the TMS spectrum shows the presence of single sextet. The parameters of this singlet are practiclly the same as for α-Fe sample. The CEMS spectrum shows the presence of α-Fe.[10]

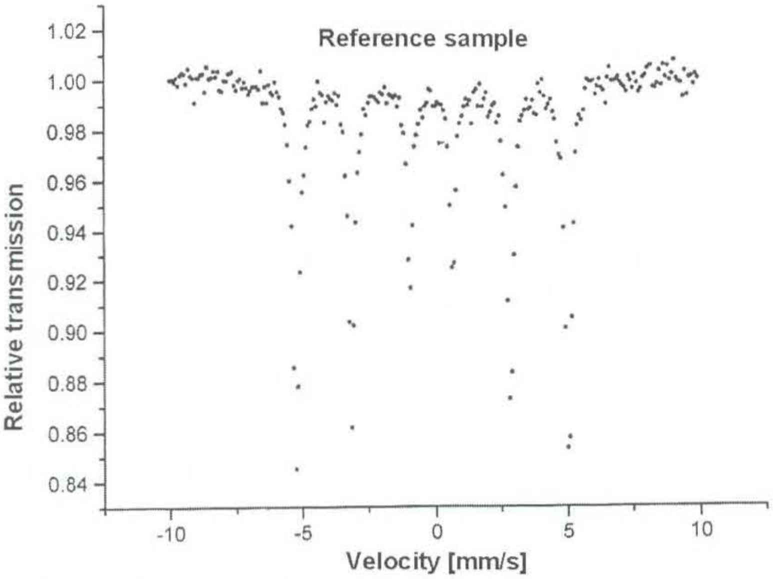

Figure 7. Transmission Mössbauer of the reference sample.

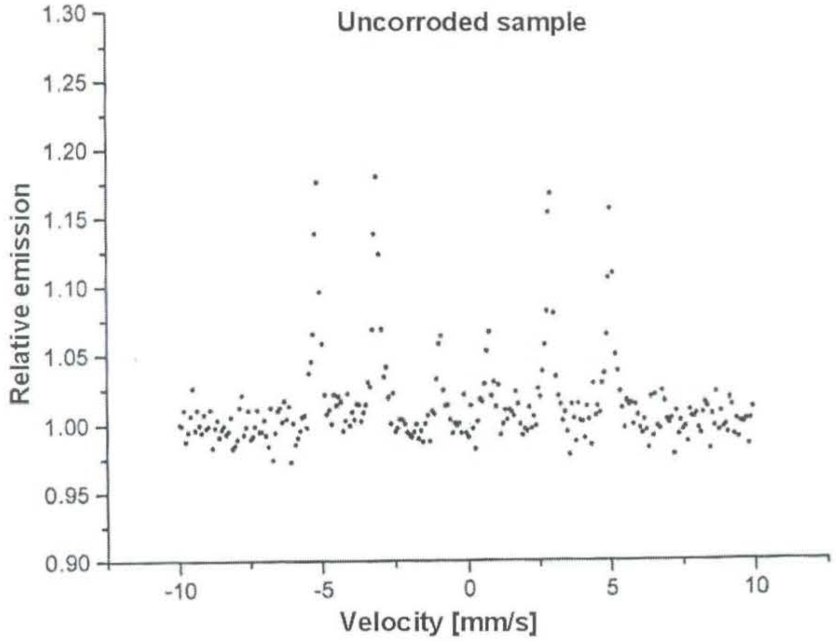

Figure 8. Conversion electron Mössbauer spectrum of an uncorroded sample.

The CEMS spectra of the sample corroded in 5 x 10^{-3} M NH_4NO_3 and 5 x 10^{-3} M NH_4Cl solutions are showed in figures 9 and 10.

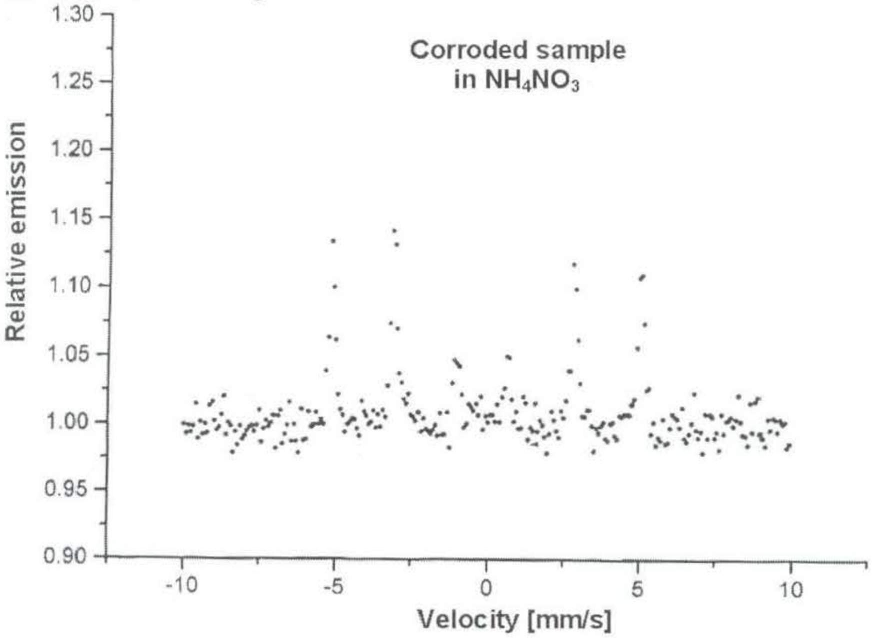

Figure 9. CEMS spectrum of corroded sample in a 5 x 10^{-3} M NH_4NO_3 solution.

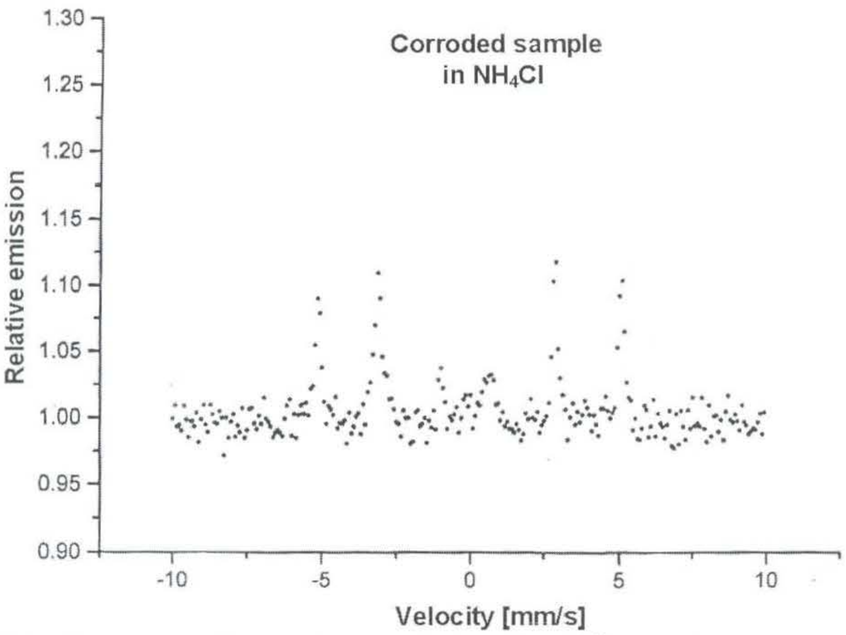

Figure 10. CEMS spectrum of corroded sample in a 5 x 10^{-3} M NH_4Cl solution.

The best fit of the CEMS spectra uses an addition wide line to the sextet. The parameters of the wide line correspond to an nonstoichiometric oxide. In all CEMS spectra intensities of the second and fifth peaks of the α-Fe spectrum with regard to the third and fourth peaks shows that the direction of the γ-ray and magnetic moments are nearly perpendicular.[11]

There is a magnetical anisotropy on the surface of the samples. The result of the corrosion is the layer appearance (nonstoichiometric iron oxide) on the samples surface. The layer tickness increases for the corroded sample in NH_4Cl solution regard to in NH_4NO_3 solution.

CONCLUSIONS

The corrosion of carbon steel in diluted ammoniacal media comes from current densities ranging between 15 mA/dm^2 and 800 mA/dm^2. The process becomes significant from densities of 130 mA/dm^2. Steel is active and dissolves after a Tafel slope b_a of 41±6 mV.

The cathodic process proceeds with a depolarization of O_2, NH_4^+, H_3O^+ and of the solvent with slopes varying from 33.3 mV to 43.3 mV.

The corrosion current increases with the increase in the NH_4Cl concentration. No metal passivation was observed during the corrosion process.

The products precipitate in solution and do not form adherent and uniform layers under which corrosion continues.

The corrosion process of carbon steel in ammonium solutions containing NO_3^- proceeds spontaneously at low current densities, the polarization curves presenting a significant slope. Current densities higher than 2 mA/dm^2 retards the process because of the passivant action of NO_3^- or because of a combined effect resulting from the synergistic action of the ammonium wit NO_3^-.

The corrosion currents are significantly smaller than in solutions containing NH_4Cl, but higher than in waters containing only dissolved ammonium. Irrespective of the NH_4NO_3 concentration they have very close values, which proves that the development of the corrosion spot is inhibited by the NO_3^- anion. The cathodic process proceeds with the depolarization of the solvent, O_2 and NH_4^+ at a Tafel slope of 32.5 mV.

Mössbauer spectroscopy shows the presence of the nonstoichiometric iron oxide layer on the samples surface. The layer tickness increases for a corroded sample in NH_4Cl solution regard to the corroded sample in NH_4NO_3 solution.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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A NEW METHOD OF COAL SEPARATION IN GRANULOMETRIC CLASSES AND THE b STUDY OF SOME ANALYTICAL PROPERTIES

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ABSTRACT

Coal is a complex heterogeneous material and for its knowledge a homogeneous fractionation is necessary. Coal presents variations in the same grains depending on density, so a more adequate fractionation is obtained by its separation according to density. The density was determined with a pycnometer and the separation of coal in different fractions according to density. The organic and inorganic solutions were replaced with distillated water.

KEYWORDS: coal, density, ash, biphasic model of coal.

RESUMO

O carvão é um material heterogêneo complexo e para o seu conhecimento é necessário um fracionamento homogêneo. O carvão apresenta variações nos mesmos grãos dependendo da densidade e consequentemente uma separação mais adequada é obtida de acordo com a densidade. A densidade foi determinada usando um picnometro e a separação do carvão em frações diferentes foi efetuada., As soluções orgânicas e inorgânicas foram substituídas com água.

PALAVRAS CHAVE: carvão, densidade, cinza, modelo bifásico para o carvão

INTRODUCTION

The methods of gravimetric separation and the obtention of coal fractions of different density with organic solvents or inorganic solutions have the disadvantage that coaly material interacts with these solutions and after separation a modified sample results with physical, chemical properties different from the initial sample.[1-3] The replacement of the organic and inorganic solutions with distilled water precludes this process.[4-12]

EXPERIMENTAL

In principle, two methods may be used to determine the density of coal, the hydrostatic balance and the pycnometer. In this paper, the density (specific volume) was determined with the pycnometer.

The determination of the coal dust density with the hydrostatic balance is impractical because of the loss of weight during the repeated sinking in distilled water.

To determine the relation between the imbibition humidity, the density and other parameters, a method must be found that permits the determination of the coal dust density and maintains the weight of the selected samples constant. The determination of the density of coal dust or grains with the help of the pycnometer satisfies these conditions. The working condition for coal grains is that the diameter of the grains to be smaller than the diameter of the pycnometer neck.

A simple pycnometer with a run in cork and a capillary hole in the middle of it was used. The determination of the coal density is based on the formula:

$$\rho_{coal} = \frac{m_{coal}}{V_{coal}}$$

where:

m_{coal} is established by subtracting the mass of the empty pycnometer from the mass of the pycnometer filled with coal.

V_{coal} is calculated from the mass of the pycnometer filled with coal and distilled water up to the mark and subtracting the mass of the empty pycnometer. The mass of the coal and the water is determined. Using the density of the water, the water volume is obtained. By; subtracting the water volume from the pycnometer volume, the coal volume is obtained.

The samples whose density was determined with the pycnometer weighed 50g and consisted of random samples (populations) of grains from sixteen different layers (XVI-stratum) of the Chiesd-Sarmasag Coal Mine. Table 1 includes the weights and densities from which the final densities of the fractions were obtained.

The determination of the ashes represents a major problem for the study of the parameters that characterize the coal. The results of the experimental results of the ashes are shown in Table 2.

Table 1: Weights and densities for the fractions of coal samples.

Fraction	Mass of the coal fraction (g)	Density (g/cm^3)	Final density (g/cm^3)
1	18,0812	1,3754	1,3810
	16,1394	1,3873	
2	17,9812	1 4032	1,4179
	19,5321	1,4317	
3	20,7042	1,4123	1,4275
	18,3548	1,4450	
4	22,7226	1,5570	1,5863
	26,2257	1,6127	
5	22,6183	1,6817	1,6833
	22,6783	1,6850	
6	19,0751	1,7513	1,7156
	17,7247	1,6788	
7	21,5738	1,7444	1,7572
	15,8049	1,7751	
8	20,8137	1,8487	1,8257
	23,5828	1 8060	
9	17,0078	2,0770	2,1031
	21,8660	2,1240	
10	22,0191	2,2033	2,1835
	18,1400	2,1600	
11	7,0400	2,2600	2,4439
	14,0212	2,4680	
	17,0212	2,5082	

Table 2: Results of the experimental determinations of the samples.

Sample	A_{anh}(%)	A_a(%)	A_1(%)
I	4,20	3,68	
II	4,20	3,69	
III	9,40	8,13	
IV	10,08	8,93	6,13
V	11,40		
VI	11,50	10,06	6,98
VII	11,70	10,35	7,22
VIII	12,80		
IX	13,30	11,67	
X	13,70		
XI	15,90		
XII	34,48	31,09	22,23
XIII	45,32	41,32	29,97
XIV	46,13	42,12	31,03
XV	46,51	42,96	32,19
XVI	57,87	53,60	40,68
XVII	72,35	67,94	52,93
XVIII	76,98	72,80	58,39
XIX	89,30	85,70	71,56

RESULTS AND DISCUSSIONS

The method for the determination of the density of coal with the pycnometer is faster and more accurate than with the use of the hydrostatic balance. It involves the use of an analytical balance and the determinations have more precision.

This method can be used for the selection of samples formed by pure grains and also to determine the density of samples selected according to certain criteria.. Using the water as a fluid medium has the advantage that it does not produce any structural modification in the coal mass and gives the opportunity, beside the rapid preparation of samples, to compare the populations of samples from different deposits of coal of the same type.

The experimental data was analyzed using the biphasic model for coal. This model includes the parameters such as the specific volume (Vsp), ash content (As%), anhydrous ash content (Aanh%) and SIO_2 content.

Table3. Experimental results for ash content (As%) and specific volume (Vsp) for coal samples studied.

Aa, %	Vspa,cm3/g			b=	-0,003885
	0,745741	0		a=	0,745741
100		0,357241		bx=	-0,00391
3,68	0,7751			R=	0,996769
3,69	0,7633			so=	0,008247
8,13	0,7352			sb=	0,000111
8,93	0,7246			sa=	0,005716
10,06	0,7092				
10,35	0,7042				
11,67	0,6896				
31,09	0,6329				
41,32	0,5952				
42,12	0,5847				
42,96	0,5714				
53,6	0,5494				
67,94	0,4761				
72,8	0,4587				
85,7	0,4098				
89,3	0,4098				
	1				

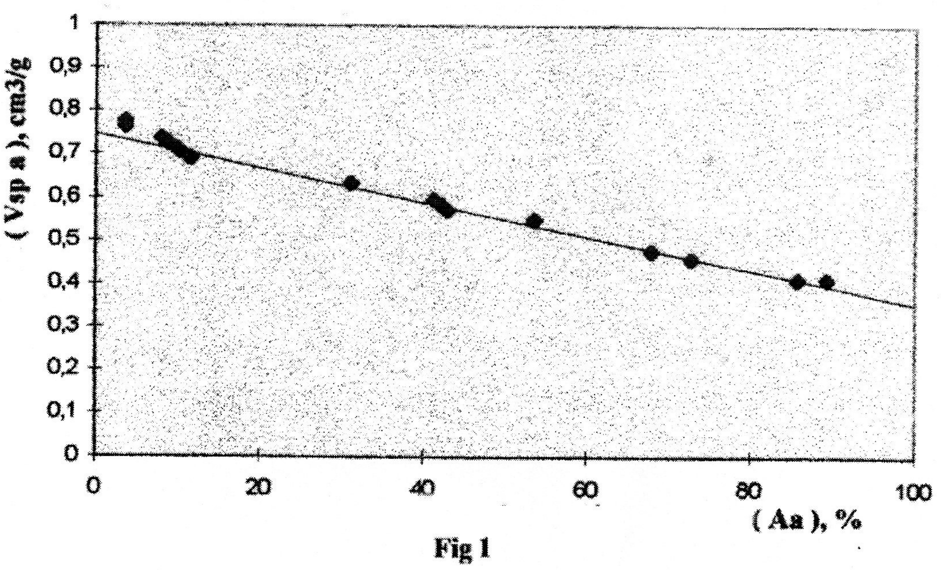

Fig 1

Figure 1. Variation of specific volume (Vsp) as a function of ash content (As%) for coal samples from the Chiesd-Sarmasag Mine.

Table 4.Experimental results for SiO_2 content and anhydrous ash content (Aanh%)

Aanh, %	SiO_2, %			b=	0,659664
	-7,81201	0		a=	-7,81201
100		58,15439		bx=	0,662669
10,08	*2,0415*			R=	0,99773
34,48	15,4402			so=	1,026617
45,32	21,1663			sb=	0,022263
57,87	30,954			sa=	1,457827
72,35	38,7225				
76,98	44,1205				
89,3	50,9559				
	70				

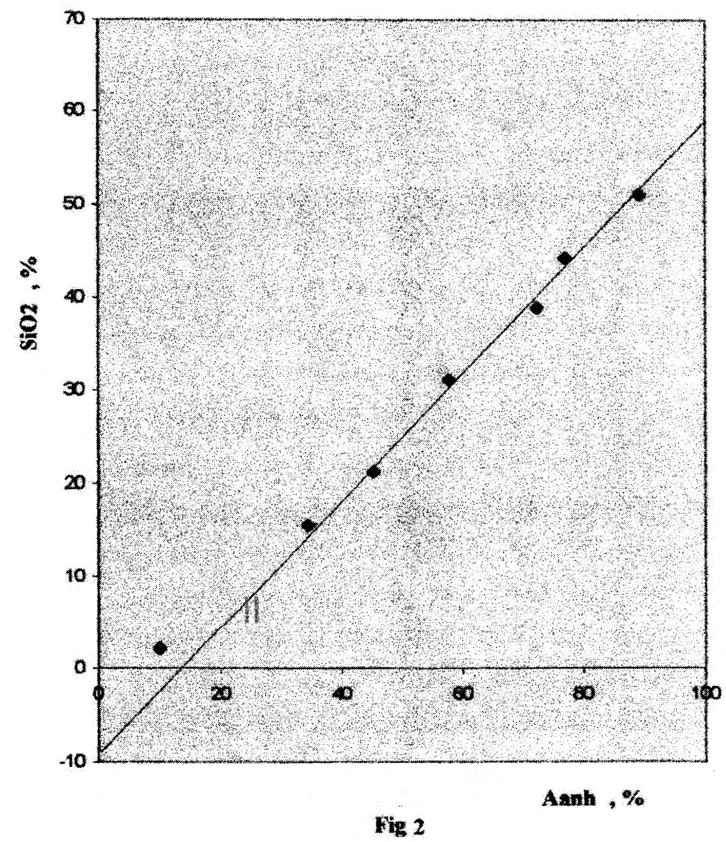

Fig 2

Figure 2. Plot of SiO_2 content as a function ash content (Aanh%)

The graphic representation of coal density in correlation with the content of anhydrous ashes is represented by a second degree curve. This shows that the density is not additive, although it doesn't vary linearly with the ashes, compared with the specific volume. Figure 1 shows the variation of the specific volume as a function of ash content of coal samples from the Chiesd-Sarmasag Coal Mine.

Considering the biphasic model for the coal, the value Aanh=11,84% (Figure 2) has an important meaning. It is obtained from the intersection of the straight line of the plot of the SiO_2 content with the axis of the ash content. Drawing the parallel to the ordinate in Figure 1we obtain the intersection of the specific volume for anhydrous (the line x=11,84%).The value of the specific volume at the intersection to is 0,6643 cm^3/g, which means that the density of the maceral part is p =1,50 g/cm^3, and extrapolated to the null ash, the density of the organic material is 1,41 g/cm^3.

The density is the parameter that has a major importance in the character of the coal complex. It depends on the petrographic composition, the uncarbonized degree, the quantity and the character of the mineral substances contained, the content of humidity and the nature of the coal.

The determination of density is very useful and it also serves for sampling research and subsequent studies. The method of determination of coal density with the pycnometer has been described in the literature for the determination of the washing liquids, which were used to fraction the mixture of coal. In this paper the method was improved, the pycnometer being used directly for the determination of the density of solid samples, both as grains with the approximate diameter of 5 mm, and as dust with the diameter of the particles of approximately 0,02 mm. The amount of work is less than in the case of the hydrostatic balance and its use in the laboratory is to be preferred, especially in the preparation of samples based on density.

Density is a valuable parameter for the study of coal. The correlations found between the specific volume and anhydrous ash, and also the $Si0_2$ content depending on the anhydrous ash, underline the validity of the biphasic model of coal as a law of nature.

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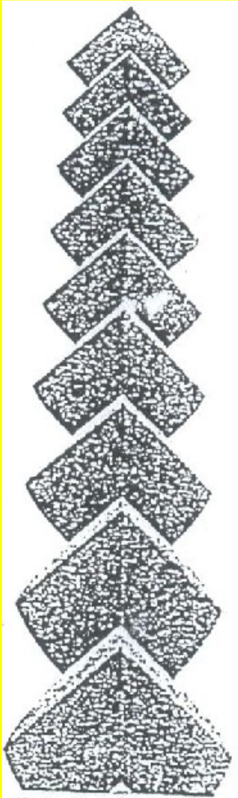

Endless Column, 1937, cast iron
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